

Article

# Six New Unsymmetrical imino-1,8-naphthalimide Derivatives Substituted at 3-C Position—Photophysical Investigations

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**Abstract:** In this research, six novel unsymmetrical imino-1,8-naphthalimides (AzNI) were synthesized. Comprehensive thermal (thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), optical (UV-Vis, photoluminescence), and electrochemical (CV, DPV) studies were carried out to characterize these new compounds. The molecules showed the onset of thermal decomposition in the temperature range 283–372 °C and molecular glass behavior. Imino-1,8-naphthalimides underwent reduction and oxidation processes with the electrochemical energy band gap ( $E_g$ ) below 2.41 eV. The optical properties were evaluated in solvents with different polarities and in the solid-state as a thin films and binary blends with poly(N-vinylcarbazole): (2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole) (PVK:PBD). Presented compounds emitted blue light in the solutions and in the green or violet spectral range in the solid-state. Their ability to emit light under external voltage was examined. The devices with guest-host structure emitted light with the maximum located in the blue to red spectral range of the electroluminescence band (EL) depending on the content of the AzNI in the PVK:PBD matrix (guest-host structure).

**Keywords:** 1,8-naphthalimide; electrochemistry; luminescence; imines

## 1. Materials and characterization methods

### 1.1. Materials

9-Anthracenecarboxaldehyde, 1-naphthaldehyde, 1-pyrenecarboxaldehyde, 4-[(2-cyanoethyl)methylamino]benzaldehyde, 4-phenyl-benzaldehyde, 4-(2-phenyleth-1-ynyl)benzaldehyde, Pd/C, 3-nitro-1,8-naphthalic anhydride, hydrazine 98%, hexylamine, poly(N-vinylcarbazole) (PVK) and 2-(4-tert-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (PBD),  $\text{Bu}_4\text{NPF}_6$ , NaOH, dichloromethane were purchased from Sigma Aldrich. Solvents (for HPLC) were purchased from Sigma Aldrich (Saint Louis, Missouri, USA). Poly(3,4(ethylenedioxy)thiophene):poly(styrenesulfonate) (PEDOT:PSS) and ITO glass were purchased from OSSILA (Sheffield, England).

### 1.2. Blends and films preparation

Films and blends on glass substrates were prepared from a homogeneous chloroform solution (10 mg/ml) of core substituted N-hexyl-1,8-naphthalimides (and with PVK:PBD (50:50 in weight %) (2 or 15 wt. % AzNIs content), respectively, by spin-coating (1000 rpm, 60s; Laurell WS 650MZ-23NPPB, North Wales, PA, USA). Films and blends

were dried for 6 h in a vacuum oven (BUCHI Glass oven B-585, Darmstadt, Germany) at 50 °C.

### 1.3. Characterization methods

Nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) spectra were recorded on a Bruker AC400 spectrometer (Berlin, Germany) in DMSO- $d_6$  (or  $\text{CDCl}_3$ ) as solvent and TMS as the internal standard. The synthesis was performed using IKA C-MAG HS7 (IKA® Poland Sp. z o.o., Warszawa, Poland) and VWR VMS-C7 (WR International, LLC.) hot plates. Infrared spectra (FTIR) were recorded on a Thermo Scientific Nicolet iS5 FT-IR Spectrometer in the range of 4000–400  $\text{cm}^{-1}$  as KBr pressed pellets (KBr before use was dried). The elementary analysis was performed using Vario EL III apparatus (Elementar, Langenselbold, Germany). Differential Scanning Calorimetry (DSC) was performed using a Du Pont 1090B apparatus (USA) with a heating/cooling rate of 20  $^{\circ}\text{C}\cdot\text{min}^{-1}$  under nitrogen and using aluminum sample pans in the range of 0–250  $^{\circ}\text{C}$ . The glass transition temperature was recorded in the second scan after cooling. Thermogravimetric analysis (TGA) was done with a Mettler Toledo TGA STARe system (Warszawa, Poland) with a heating rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$  in a constant stream of nitrogen (20  $\text{ml}\cdot\text{min}^{-1}$ ) and a temperature range from 25  $^{\circ}\text{C}$  to 600  $^{\circ}\text{C}$ . UV-Vis absorption spectra were performed using an Evolution 220 UV-Visible Spectrophotometer (London, United Kingdom) as the concentration of  $10^{-5}$  mol/L and 1 cm quartz cell and Jasco V-550 Spectrophotometer (Easton, MD 21601) for films and blends. Photoluminescence spectra (PL) in solutions were performed by using Varian Carry Eclipse Spectrometer (Santa Clara, US) and using Hitachi F-2500 Spectrometer (Berkshire, United Kingdom) for blends and films PL measurements. Quantum yields ( $\Phi_f$ ) measurements were performed by using the integrating sphere Avantes AvaSphere-80 (Edinburgh Instruments, Austin TX, US) and absolute method. The lifetime ( $\tau$ ) of photoluminescence was measured with a time-correlated single photon counting (TCSPC). The time-resolved measurements were performed using the picosecond pulsed diode laser, EPL-340 nm using a 60 W microsecond Xe flash lamp (Edinburgh Instruments, Austin TX, US). Pulse period for all measurements was equal to 50 ns and PMT (Hamamatsu, R928P, Shimokanzo, Iwata City, Japan) as a detector. The fluorescence decay analysis was received an instrument response function (IRF) using ludox solution and results were presented as average values of decay after exponential fitting. Electrochemical measurements (CV) were performed with Eco Chemie Autolab PGSTAT128n potentiostat (Metrohm Autolab B.V. The Netherlands). A platinum wire (diam. 1.0 mm) served as a working electrode, while platinum coil and silver wire were used as auxiliary and reference electrode respectively. All potentials were referenced with respect to the stable internal standard, which was ferrocene couple ( $\text{Fc}/\text{Fc}^+$ ). Electrochemical experiments were conducted in a one-compartment cell, in  $\text{CH}_2\text{Cl}_2$  (ACROSS Organics, 99.9% for biochemistry grade, Janssen Pharmaceutica, Belgium) and dry ACN (Acetonitrile, Sigma Aldrich for HPLC, gradient grade >99.9%, (Saint Louis, Missouri, USA) under argon purging, with 0.1M  $\text{Bu}_4\text{NPF}_6$  (Aldrich, 99%, (Saint Louis, Missouri, USA) used as the supporting electrolyte salt. Each experiment was performed in an air-conditioned room in stable temperature ( $t = 20\text{ }^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ).

### 1.4. Theoretical calculations

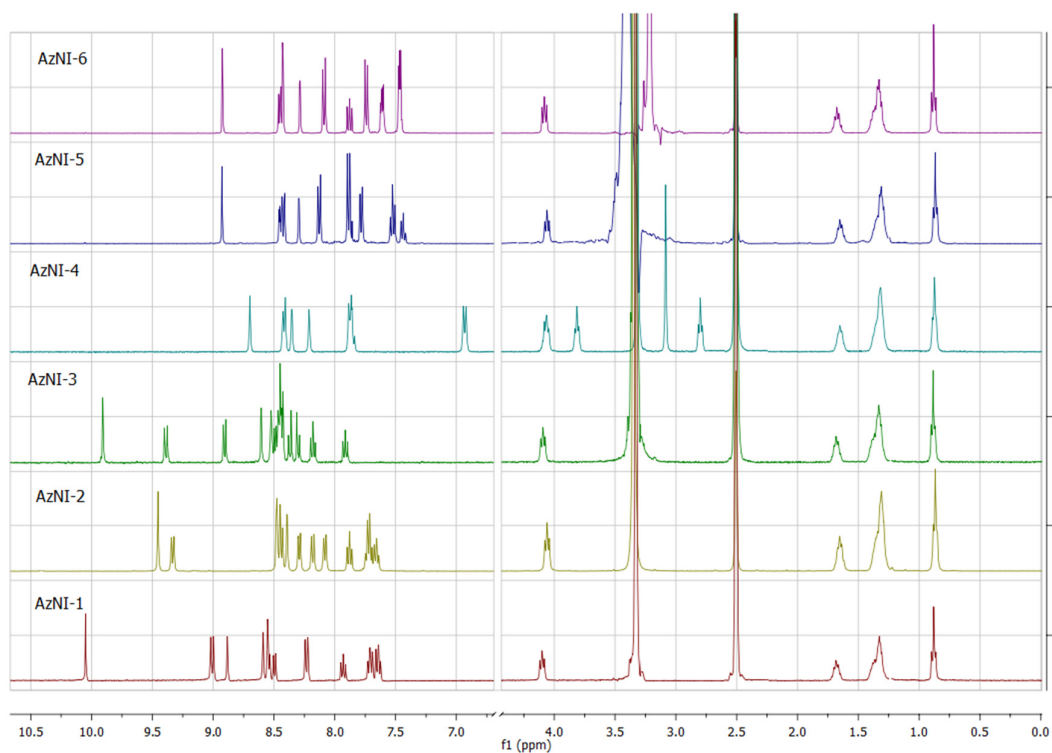
The theoretical calculations were performed with the use of the density functional theory (DFT) and were carried out using the Gaussian09 program (C.01, Gaussian, Inc., Wallingford CT, 2019) [1] on B3LYP/6-31g(d,p) level [2,3] augmented with GD3BJ dispersion correction model [4]. Molecular geometry of the singlet ground state of the compounds was optimized in the gas phase and the frequency calculation for each of the compounds shows only positive values which verify that the optimized molecular structure corresponds to energy minimum. Solvent effect was taken into account using polarizable continuum model (PCM) [5] with dichloromethane and chloroform as solvents. Such calculations were carried out for analysis of the frontier molecular orbitals

structure, energy levels and UV-Vis data. Density of states diagrams were obtained with use of GaussSum program (2.2, city, country) [6]. The TD-DFT (time dependent density functional theory) method [7] was employed to calculate the electronic absorption spectra of the compounds in solvents and geometries and energies in singlet/triplet excited states.

### 1.5. OLED preparation and electroluminescence measurements

Devices with sandwich configuration ITO/PEDOT:PSS/AzNI/Al and ITO/PEDOT:PSS/AzNI:PVK:PBD/Al with 2 and 15 wt. % of AzNIs content in blend were prepared. Devices were prepared on OSSILA substrates with pixilated ITO anodes, cleaned with detergent, deionized water, 10% NaOH solution, water and isopropyl alcohol in an ultrasonic bath. Substrates were covered with PEDOT:PSS film by spin coating at 5000rpm for 60s and annealed for 5 min at 120°C. Active layer was spin-coated on top of the PEDOT:PSS layer from chloroform solution (10 mg/mL) at 1000 rpm for 60 s and annealed for 5 min at 100°C. Finally, Al was vacuum-deposited at a pressure of  $5 \cdot 10^{-5}$  Torr. Electroluminescence (EL) spectra were measured with the voltage applied using a precise voltage supply (GwInstek PSP-405, Taipei, Taiwan) and the sample was fixed to an XYZ stage. Light from the OLED device was collected through a 30mm lens, focused on the entrance slit (50 $\mu$ m) of a monochromator (Shamrock SR-303i, Andor Technology, Belfast, Ireland) and detected using a CCD detector (AndoriDus 12305, Oxford Instruments, London). Typical acquisition times were equal to 10 s. The pre-alignment of the setup was done using a 405 nm laser. At this stage, the diode parameters (luminance, luminous efficacy) were not measured.

## 2. NMR spectra



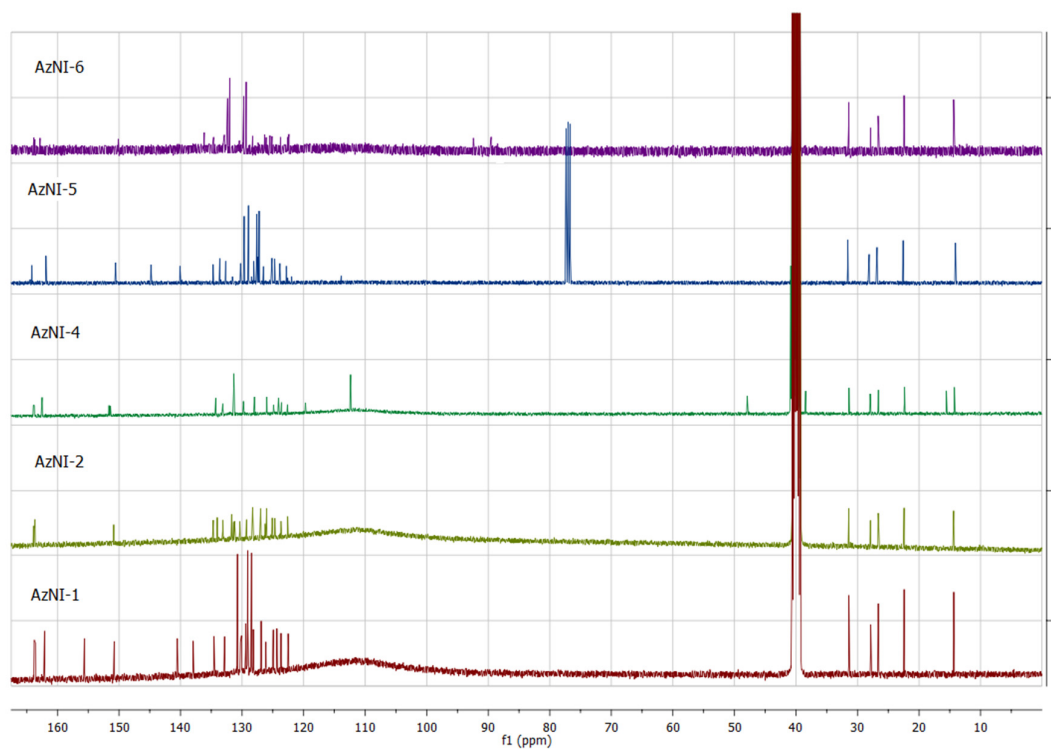
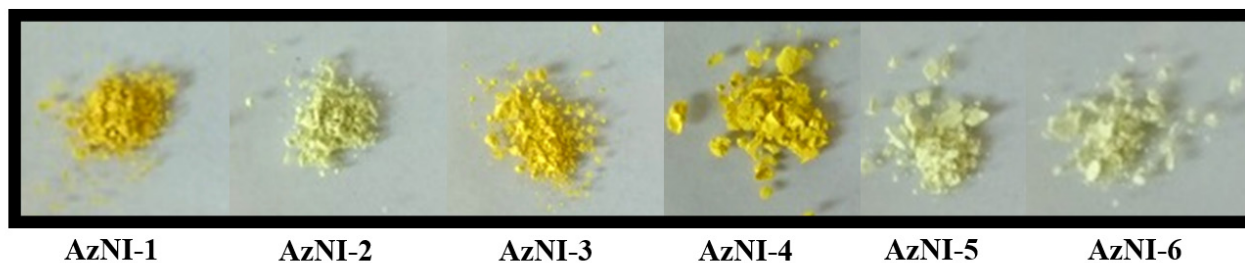


Figure S1.  $^1\text{H}$  NMR(DMSO- $d_6$ , 400MHz) and  $^{13}\text{C}$  NMR spectra (DMSO- $d_6$  or  $\text{CDCl}_3$ , 101MHz).

### 3. Photographs of the solid state of AzNIs

*Under daylight*



*Under UV irradiation ( $\lambda_{ex} = 366 \text{ nm}$ )*

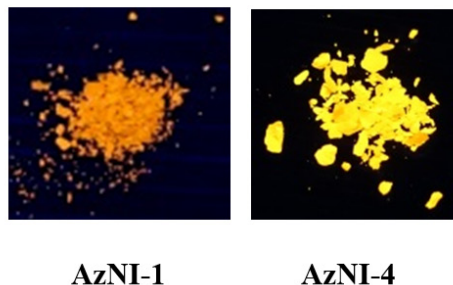


Figure S2. Photographs of the solid state of AzNIs under daylight and under UV irradiation.

#### 4. Thermal investigations

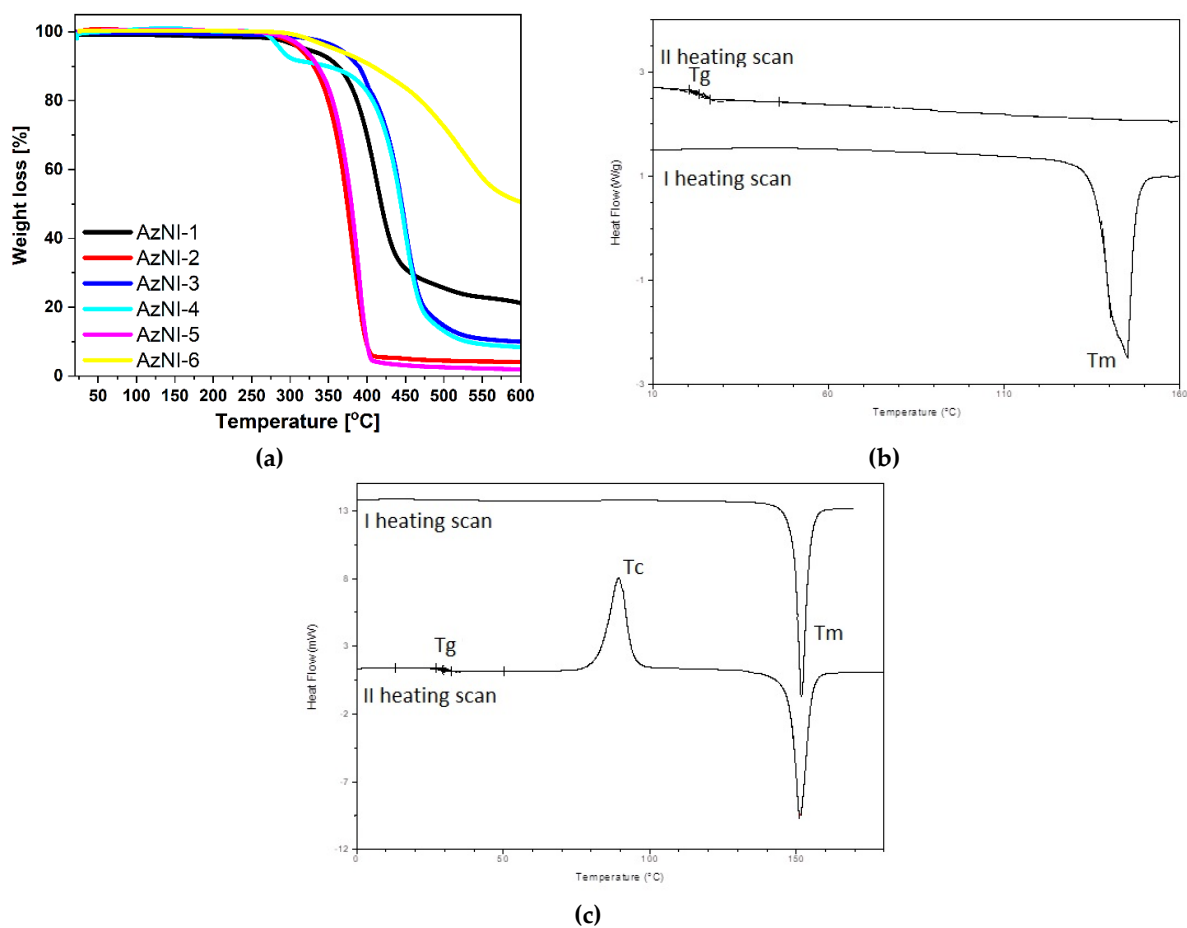
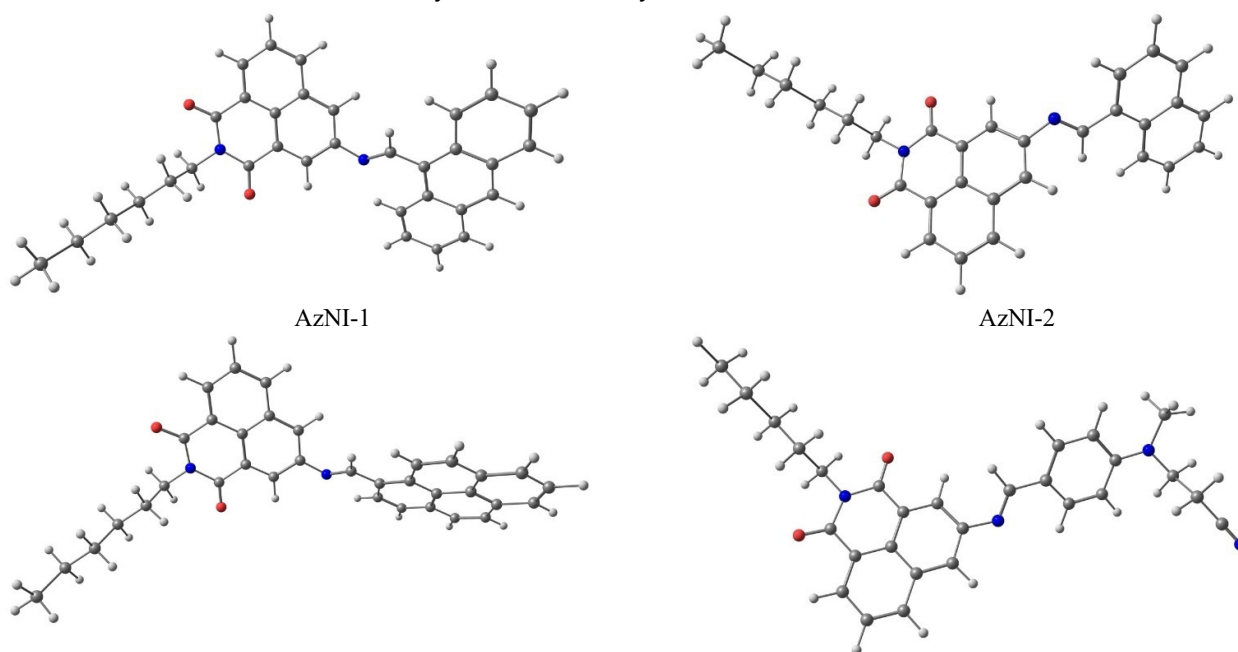
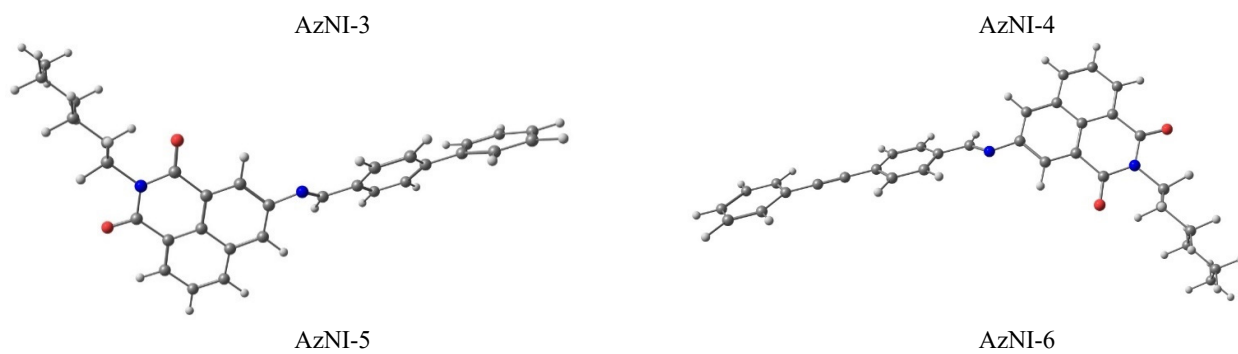


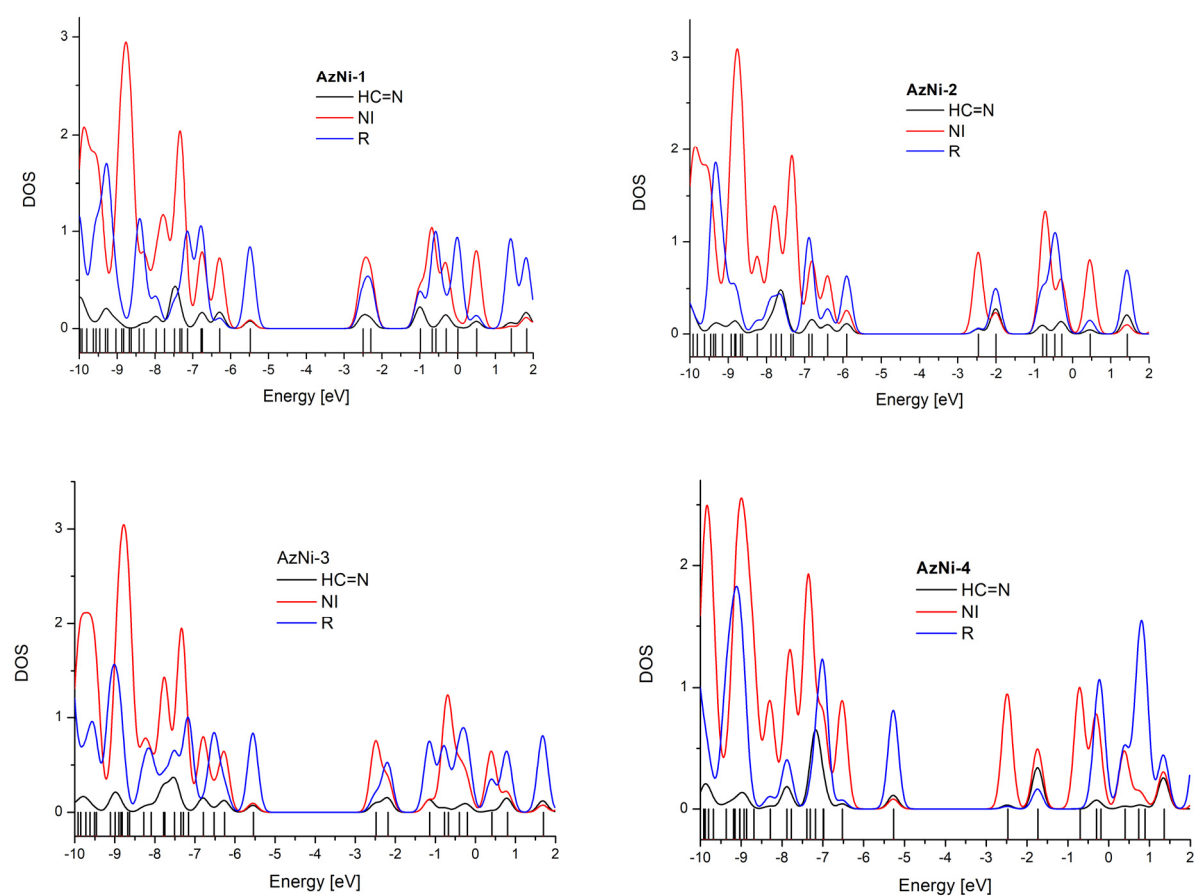
Figure S3. (a) TGA thermograms and DSC thermograms of (b) AzNI-5 and (c) AzNI-6.

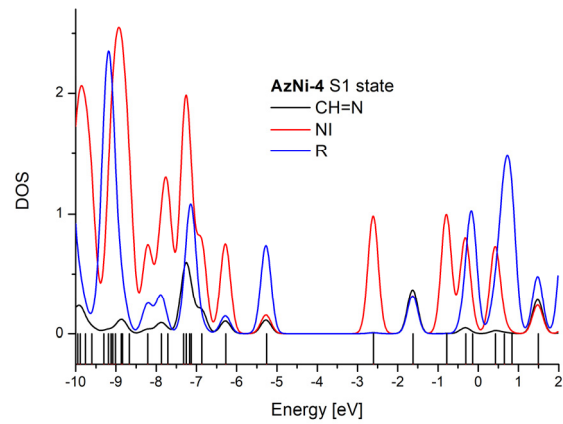
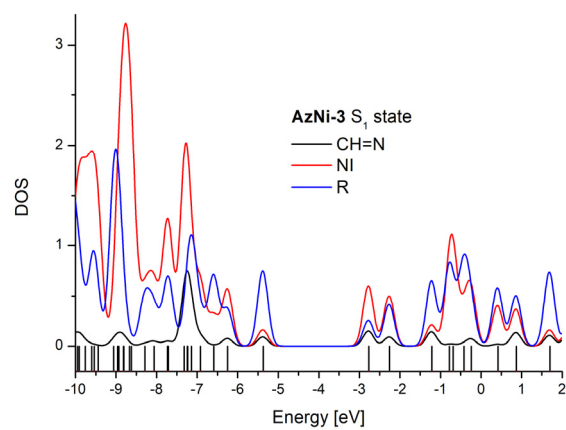
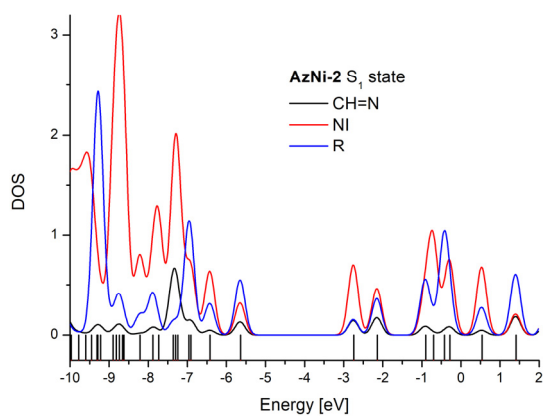
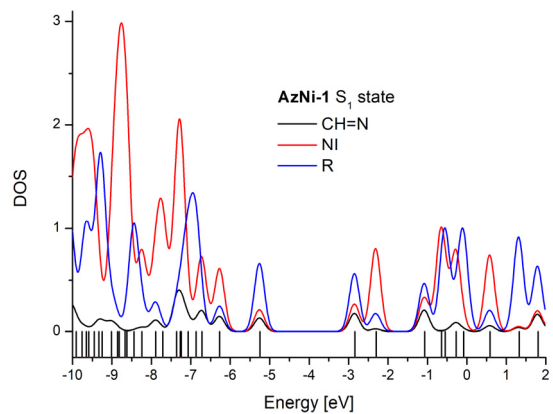
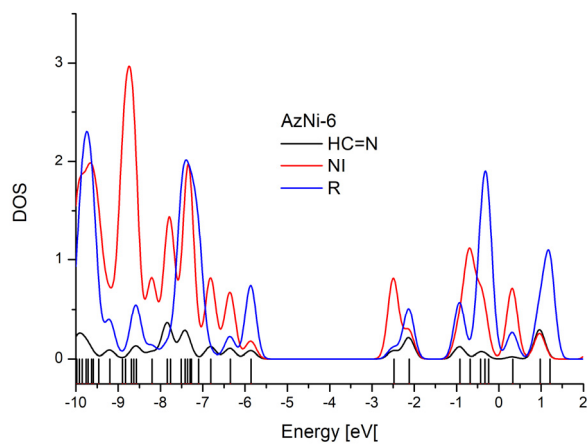
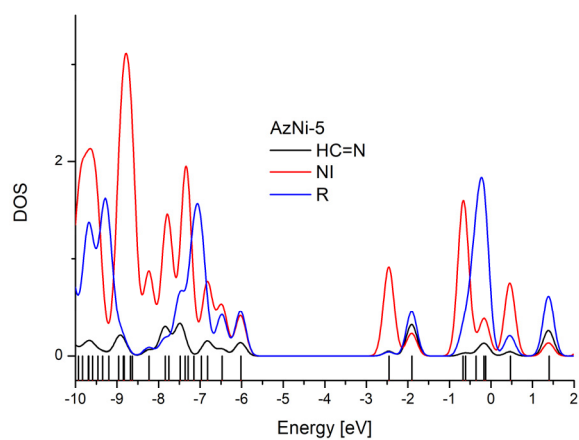
#### 5. Density functional theory calculations

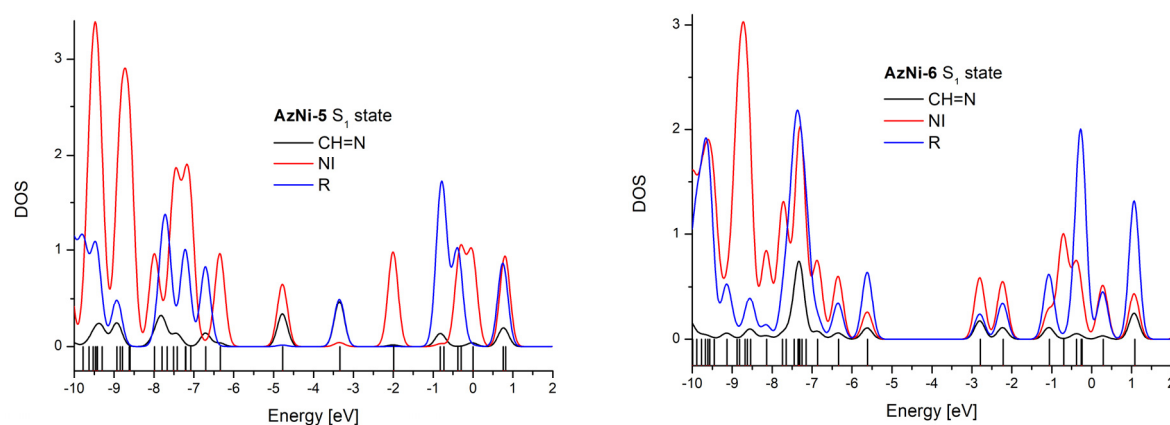




**Figure S4.** Optimized geometries of the compounds AzNI.







**Figure S5.** Density-of-states diagrams. NI: N-hexyl-1,8-naphthalimide; R: 9-anthracene, 1-naphthalene, 1-pyrene, 4-[(2-cyanoethyl)methylamino]-4-benzene, 4-phenyl-benzene, 4-(2-phenyleth-1-ynyl)benzene in AzNI-1, AzNI-2, AzNI-3, AzNI-4, AzNI-5, and AzNI-6, respectively.

**Table S1.** Ground and  $S_1$  state composition of selected molecular orbitals.

#### GS

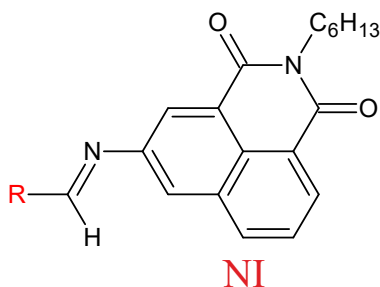
AzNI-1	eV	CH=N	NI	R	AzNI-2	eV	CH=N	NI	R
L+5	−0.30	14	66	20	L+5	−0.28	13	58	29
L+4	−0.57	0	2	98	L+4	−0.46	1	3	96
L+3	−0.67	0	100	0	L+3	−0.68	0	99	0
L+2	−0.98	22	41	37	L+2	−0.78	9	43	48
L+1	−2.29	8	50	42	L+1	−2.00	27	23	50
LUMO	−2.50	11	55	34	LUMO	−2.46	5	89	6
HOMO	−5.48	7	8	84	HOMO	−5.90	11	25	64
H-1	−6.29	17	73	10	H-1	−6.40	10	63	27
H-2	−6.75	14	67	19	H-2	−6.81	15	79	6
H-3	−6.78	2	12	86	H-3	−6.89	0	0	100
H-4	−7.14	0	3	97	H-4	−7.30	0	100	0
H-5	−7.29	0	100	0	H-5	−7.36	2	98	0
AzNI-3	eV	CH=N	NI	R	AzNI-4	eV	CH=N	NI	R
L+5	−0.40	4	39	57	L+5	0.41	2	73	25
L+4	−0.67	0	100	0	L+4	−0.25	0	9	91
L+3	−0.77	4	27	68	L+3	−0.36	5	74	21
L+2	−1.14	13	13	74	L+2	−0.64	0	100	0
L+1	−2.18	15	34	52	L+1	−1.61	38	29	33
LUMO	−2.48	9	73	18	LUMO	−2.40	2	97	1
HOMO	−5.54	7	9	84	HOMO	−5.46	10	15	74
H-1	−6.26	12	62	26	H-1	−6.28	14	70	16
H-2	−6.52	2	18	80	H-2	−6.83	12	83	5
H-3	−6.79	15	78	8	H-3	−7.10	0	0	99
H-4	−7.16	1	0	99	H-4	−7.27	7	91	2
H-5	−7.29	0	100	0	H-5	−7.36	5	95	0
AzNI-5	eV	CH=N	NI	R	AzNI-6	eV	CH=N	NI	R
L+5	−0.17	5	14	80	L+5	−0.33	3	26	72
L+4	−0.36	1	2	97	L+4	−0.43	5	43	52
L+3	−0.61	3	66	31	L+3	−0.68	0	100	0
L+2	−0.67	0	99	0	L+2	−0.92	12	31	57
L+1	−1.90	32	23	45	L+1	−2.12	21	28	50
LUMO	−2.45	5	91	4	LUMO	−2.48	8	81	11
HOMO	−6.02	13	41	46	HOMO	−5.86	8	18	74

H-1	−6.47	7	51	42	H-1	−6.35	10	67	22
H-2	−6.82	15	75	10	H-2	−6.81	12	82	6
H-3	−6.97	0	0	100	H-3	−7.10	0	0	100
H-4	−7.15	0	0	100	H-4	−7.27	1	1	98
H-5	−7.29	0	100	0	H-5	−7.30	0	98	2

**S<sub>1</sub> state**

<b>AzNI-1</b>	eV	CH=N	NI	R	<b>AzNI-2</b>	eV	CH=N	NI	R
L+5	−0.27	8	77	15	L+5	−0.28	8	71	21
L+4	−0.55	0	2	98	L+4	−0.42	1	7	92
L+3	−0.64	0	99	1	L+3	−0.70	1	92	7
L+2	−1.07	20	33	47	L+2	−0.90	8	38	54
L+1	−2.30	2	80	17	L+1	−2.14	17	46	36
LUMO	−2.84	17	26	56	LUMO	−2.74	14	70	15
HOMO	−5.25	13	21	66	HOMO	−5.64	13	32	55
H-1	−6.27	14	61	24	H-1	−6.42	5	64	31
H-2	−6.72	20	72	8	H-2	−6.91	13	62	25
H-3	−6.87	0	0	100	H-3	−6.96	1	7	91
H-4	−7.07	10	9	81	H-4	−7.24	0	100	0
H-5	−7.24	1	98	1	H-5	−7.30	38	57	5
<b>AzNI-3</b>	eV	CH=N	NI	R	<b>AzNI-4</b>	eV	CH=N	NI	R
L+5	−0.42	1	25	74	L+5	0.43	2	71	27
L+4	−0.69	1	83	16	L+4	−0.14	0	5	95
L+3	−0.78	1	31	68	L+3	−0.31	5	78	18
L+2	−1.21	14	21	65	L+2	−0.78	0	100	0
L+1	−2.26	9	50	41	L+1	−1.62	37	32	32
LUMO	−2.77	15	60	25	LUMO	−2.60	1	99	1
HOMO	−5.37	9	16	75	HOMO	−5.26	11	15	73
H-1	−6.25	7	57	36	H-1	−6.27	11	75	15
H-2	−6.59	1	29	70	H-2	−6.87	19	74	7
H-3	−6.92	9	63	28	H-3	−7.13	2	1	97
H-4	−7.14	3	3	94	H-4	−7.17	15	79	6
H-5	−7.23	11	87	2	H-5	−7.25	36	59	6
<b>AzNI-5</b>	eV	CH=N	NI	R	<b>AzNI-6</b>	eV	CH=N	NI	R
L+5	−0.30	0	96	4	L+5	−0.26	1	20	79
L+4	−0.38	0	3	97	L+4	−0.38	4	58	37
L+3	−0.73	3	1	96	L+3	−0.70	0	97	2
L+2	−0.82	11	2	87	L+2	−1.06	11	27	62
L+1	−1.99	2	98	0	L+1	−2.22	11	55	34
LUMO	−3.34	47	4	49	LUMO	−2.79	17	59	24
HOMO	−4.77	34	65	2	HOMO	−5.61	11	26	64
H-1	−6.34	4	96	0	H-1	−6.34	6	60	34
H-2	−6.70	14	3	83	H-2	−6.86	7	74	19
H-3	−7.08	0	100	0	H-3	−7.15	0	0	100
H-4	−7.20	0	98	2	H-4	−7.25	1	99	0
H-5	−7.21	0	2	98	H-5	−7.31	63	16	22

NI: N-hexyl-1,8-naphthalimide; R: 9-anthracene, 1-naphthalene, 1-pyrene, 4-[(2-cyanoethyl)methylamino]-4-benzene, 4-phenyl-benzene, 4-(2-phenyleth-1-ynyl)benzene in AzNI-1, AzNI-2, AzNI-3, AzNI-4, AzNI-5, and AzNI-6, respectively.

**Table S2.** Calculated, in the chloroform solution, dipole moments and mean plane angles for the imine molecules.

Dipole moment (D)			Dipole moment (D)		
$\angle$ NI-R (°)			$\angle$ NI-R (°)		
AzNI-1			AzNI-4		
S <sub>0</sub>	7.30	28.72	S <sub>0</sub>	5.97	35.51
S <sub>1</sub>	8.59	32.67	S <sub>1</sub>	7.00	22.61
T <sub>1</sub>	9.02	30.74	T <sub>1</sub>	4.49	53.76
AzNI-2			AzNI-5		
S <sub>0</sub>	7.12	47.71	S <sub>0</sub>	7.19	44.38
S <sub>1</sub>	7.93	10.48	S <sub>1</sub>	15.84	85.67
T <sub>1</sub>	8.40	2.23	T <sub>1</sub>	8.25	0.52
AzNI-3			AzNI-6		
S <sub>0</sub>	8.01	45.45	S <sub>0</sub>	7.28	43.85
S <sub>1</sub>	8.98	6.15	S <sub>1</sub>	8.05	6.06
T <sub>1</sub>	9.82	3.15	T <sub>1</sub>	8.43	1.88

**Table S3.** The calculated electronic transitions corresponding to excitation wavelength in CHCl<sub>3</sub> solution.

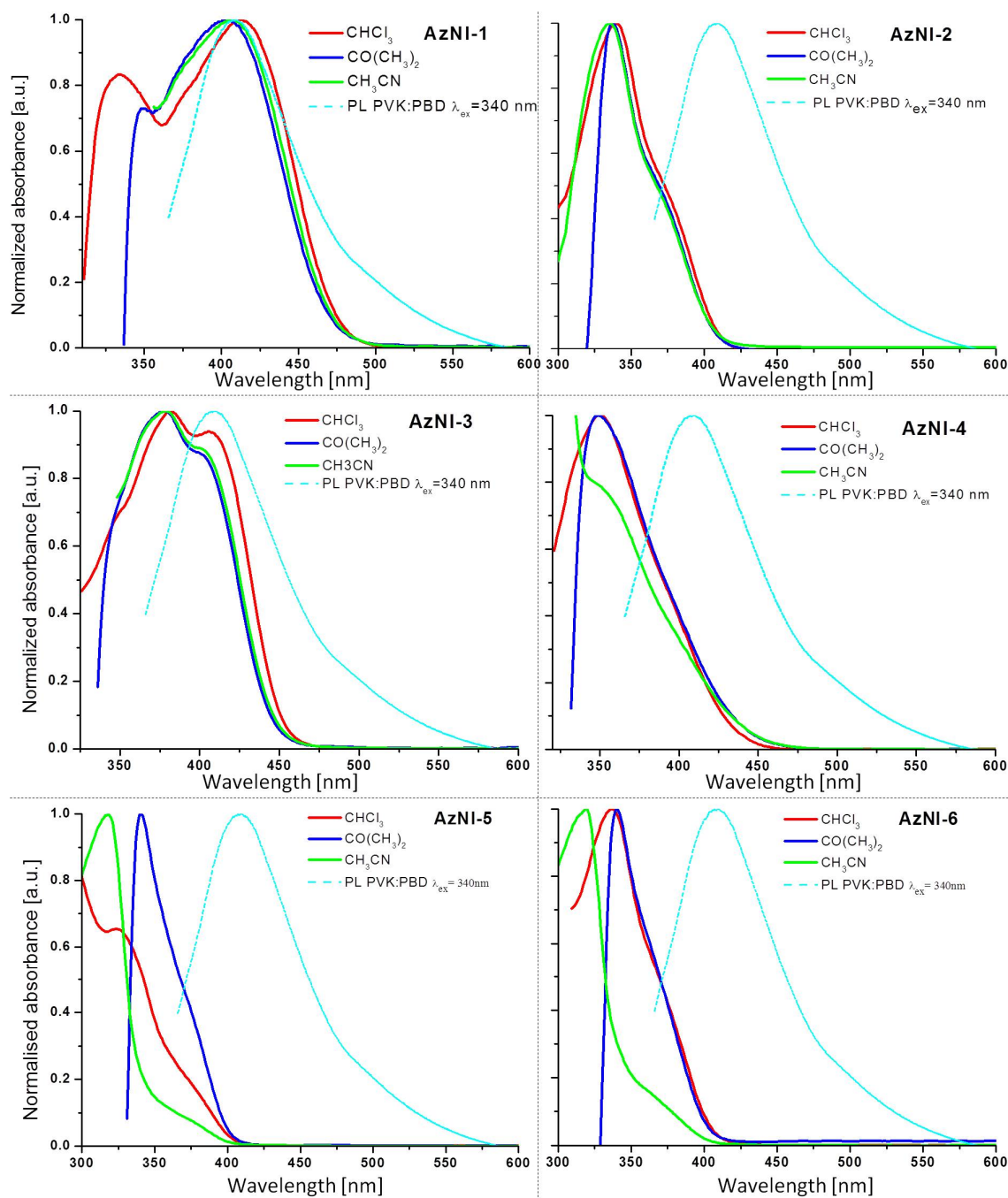
	$\lambda_{exp}$	$\lambda_{calc}$ (f)	transition	character
AzNI-1	411	437.7 (0.2159)	HOMO→L+1 (97%)	$\pi_R \rightarrow \pi^*_{R/NI}$
	331	336.1 (0.1660)	H-3→LUMO (39%); H-2→LUMO (30%)	$\pi_{R/NI} \rightarrow \pi^*_{R/NI}$
AzNI-2	338	332.4 (0.1637)	H-2→LUMO (70%)	$\pi_{NI} \rightarrow \pi^*_{NI}$
AzNI-3	405	406.4 (0.7709)	HOMO→L+1 (92%)	$\pi_R \rightarrow \pi^*$
	381	368.6 (0.1012)	H-1→LUMO (77%)	$\pi_{NI} \rightarrow \pi^*_{NI}$
AzNI-4	349	360.9 (0.9193)	HOMO→L+1 (94%)	$\pi_R \rightarrow \pi^*_{R/HC=N}$
		355.5 (0.1237)	H-1→LUMO (93%)	$\pi_{NI} \rightarrow \pi^*_{NI}$
AzNI-5	340	349.8 (0.6645)	HOMO→L+1 (84%)	$\pi \rightarrow \pi^*$
	323	327.9 (0.1928)	H-2→LUMO (82%)	$\pi_{NI} \rightarrow \pi^*_{NI}$
AzNI-6	335	337.2 (0.1928)	H-2→LUMO (48%); H-1→L+1 (42%)	$\pi_{NI} \rightarrow \pi^*_{NI}$

**Table S4.** Energy differences between excited states.

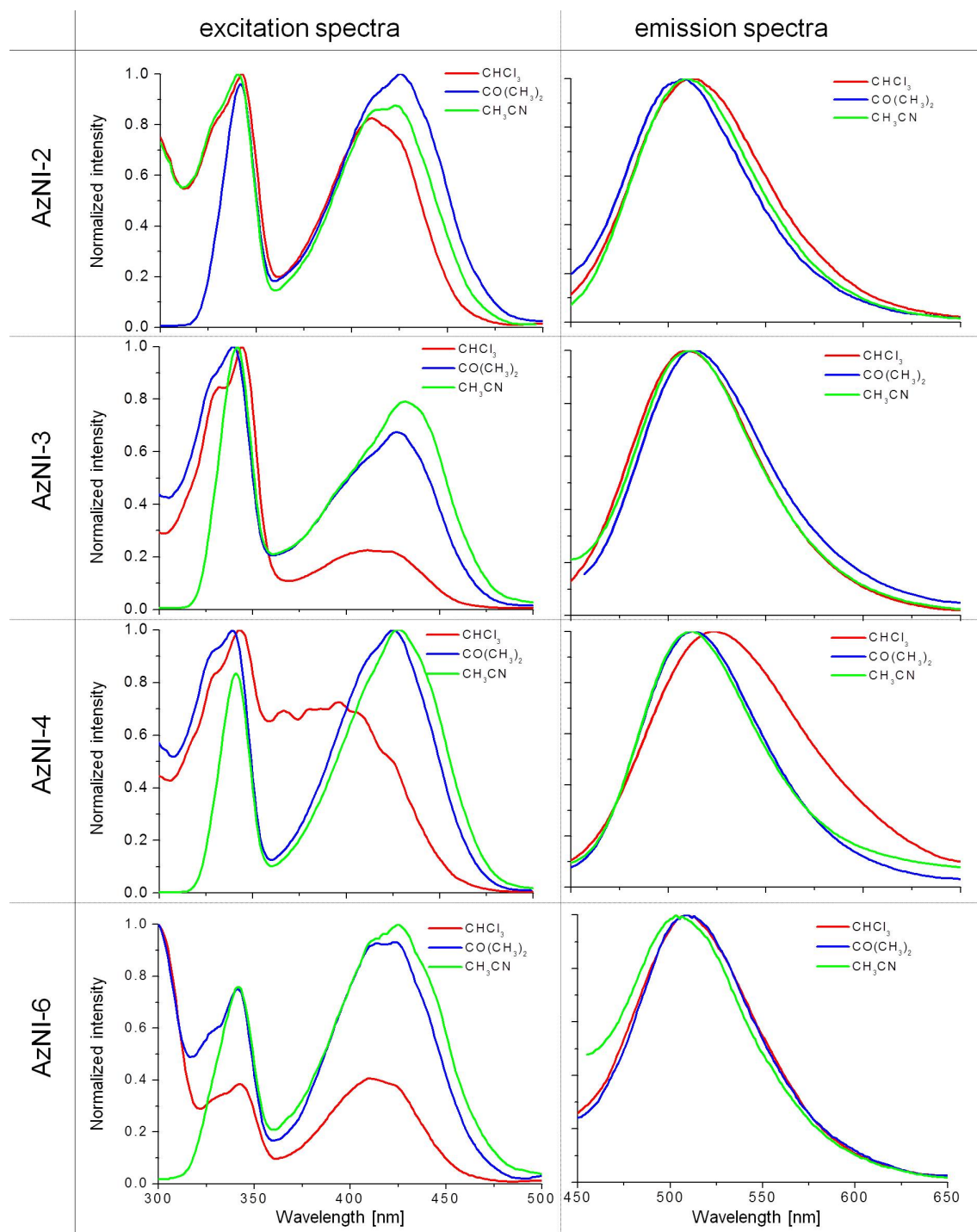
	AzNI-1	AzNI-2	AzNI-3	AzNI-4	AzNI-5	AzNI-6
$\phi E_{(S_0-S_1)}(nm)$	534 (511)*	452 (511)	504 (509)	514 (523)	581 (511)	460 (508)
$\phi E_{(T_1-S_0)}(cm^{-1})$	4399	12731	11870	6539	13943	13313
$\phi E_{(T_1-S_1)}(cm^{-1})$	2806	2805	3242	3975	3268	3134
$\phi E_{(T_2-S_1)}(cm^{-1})$	3146	4686	7959	1940	1875	4107
$\phi E_{(T_2-T_1)}(cm^{-1})$	11173	4690	8872	10322	5143	4324

\* in parenthesis are given experimental values of emission maxima.

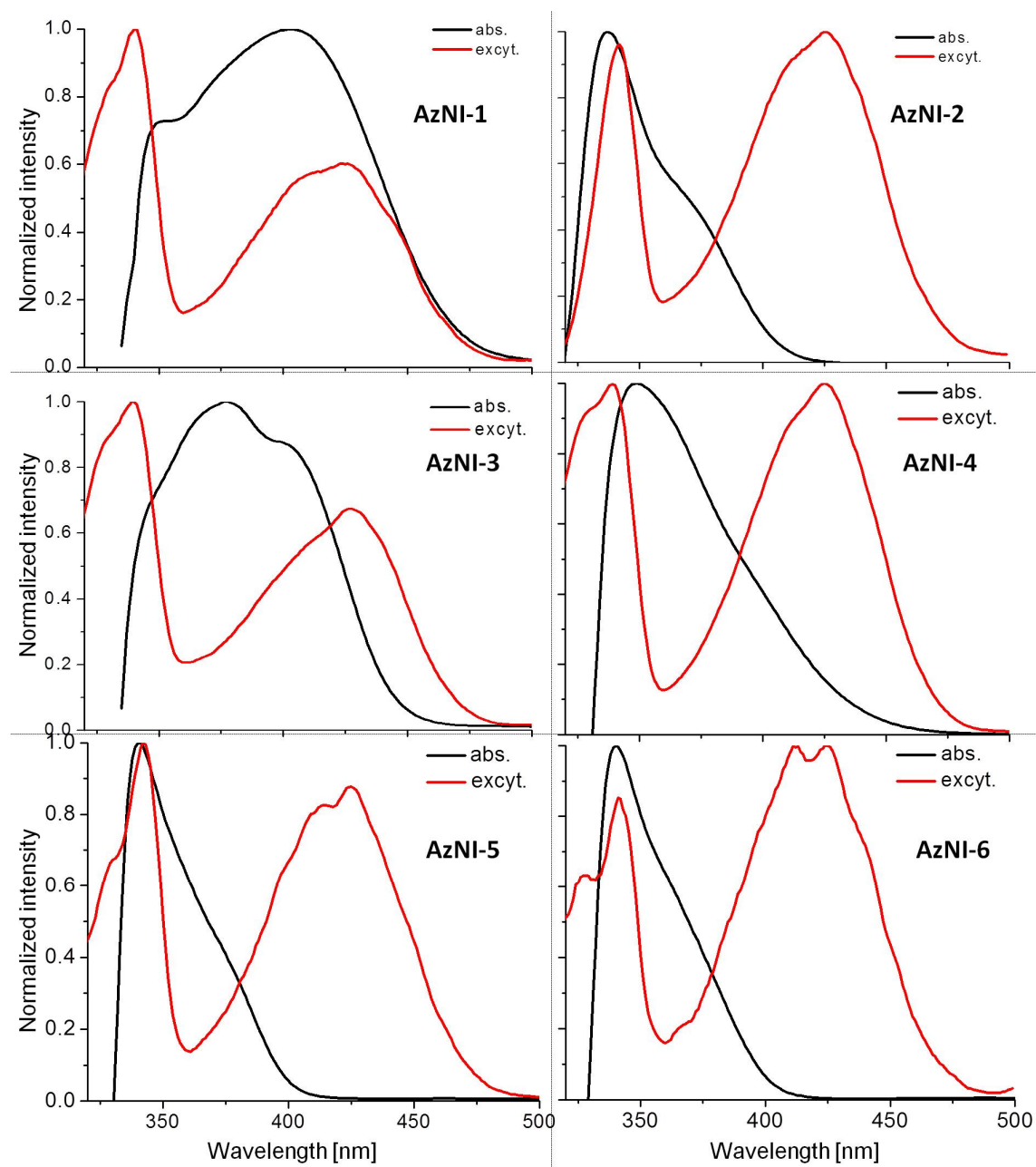
### 6. Optical properties



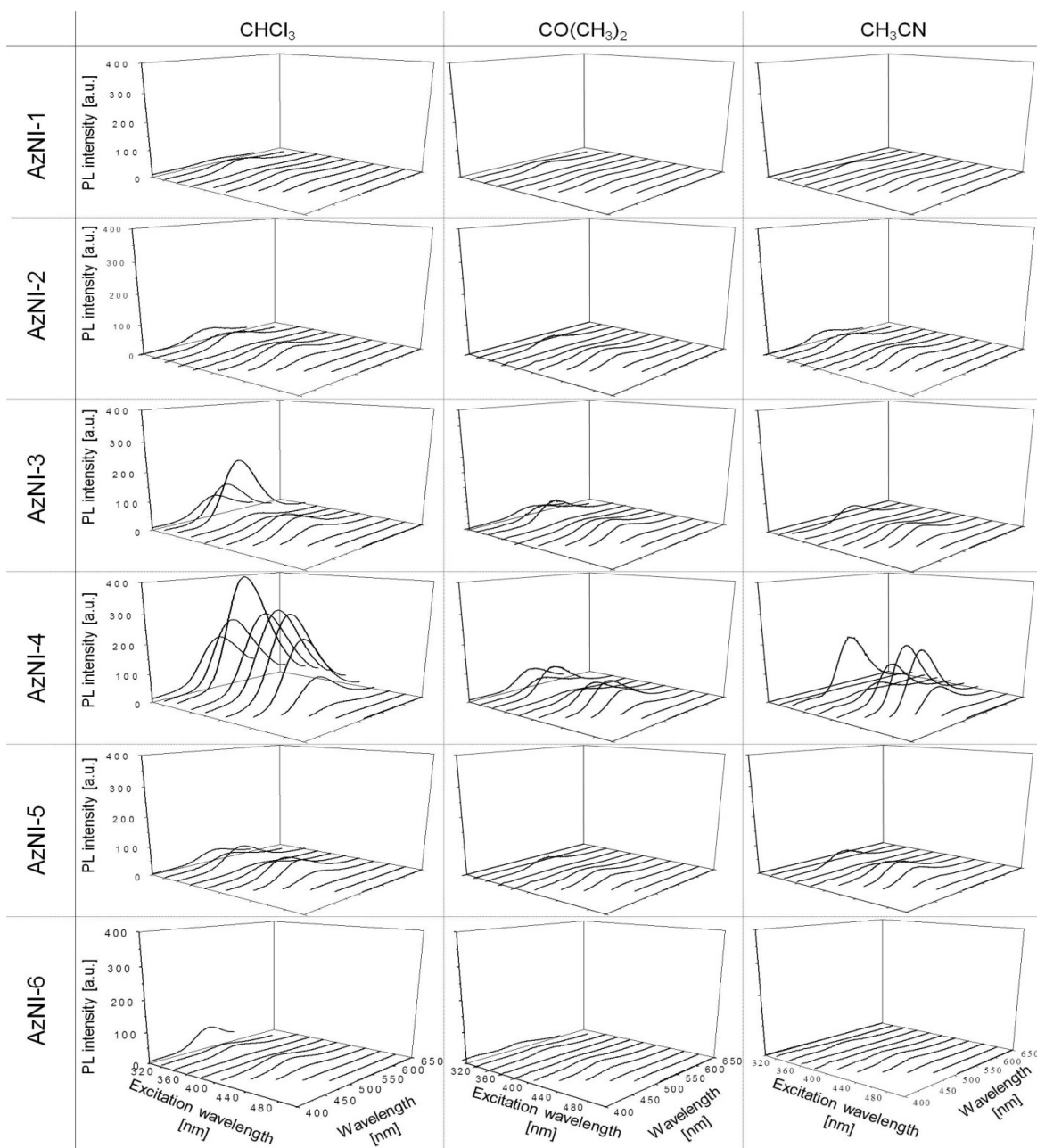
**Figure S6.** The absorption spectra of the *N*-hexyl-1,8-naphthalimides derivatives (AzNI-1 - 6) in the various solvents with the emission spectra of the PVK:PBD matrix.



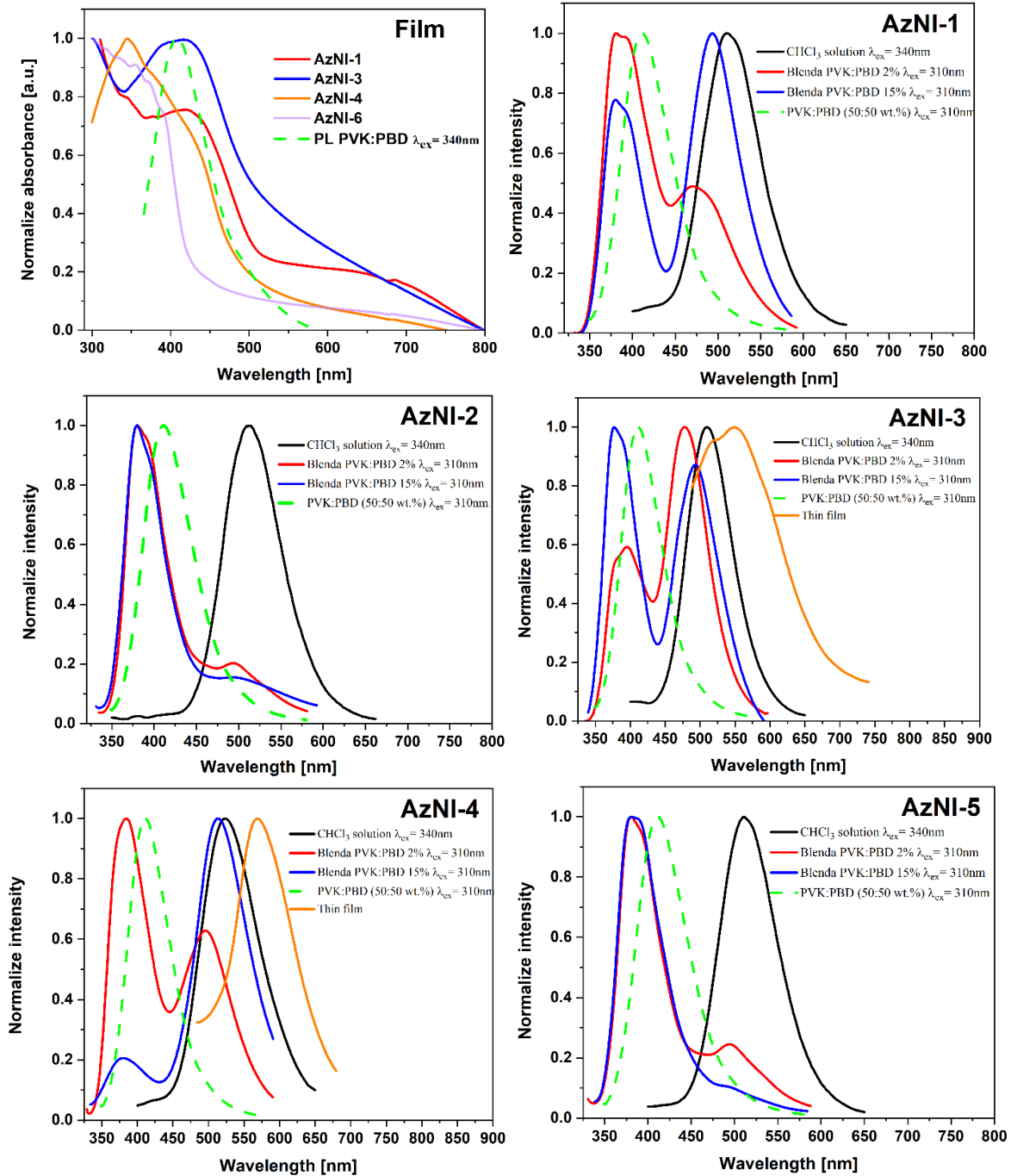
**Figure S7.** The excitation and emission spectra of the *N*-hexyl-1,8-naphthalimides derivatives (AzNI- 2, 3, 4, 6) in the various solvents ( $\lambda_{\text{ex}} = 340 \text{ nm}$ ).

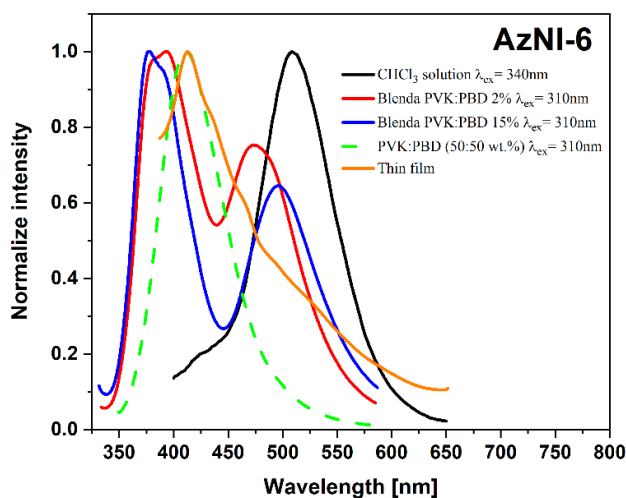


**Figure S8.** The absorption and excitation spectra of the *N*-hexyl-1,8-naphthalimides derivatives (AzNI- 1- 6) in acetone.



**Figure S9.** The 3D fluorescence spectra of the analyzed compounds in the excitation range from 300 to 500 nm and the collected emissions in the range from 400 to 650 nm in the chloroform ( $\text{CHCl}_3$ ), acetone ( $\text{CO}(\text{CH}_3)_2$ ) and acetonitrile ( $\text{CH}_3\text{CN}$ ). Measurements were performed for equal concentration of each compound ( $c = 1 \cdot 10^{-5} \text{ mol/dm}^3$ ) and under the same measurement conditions.



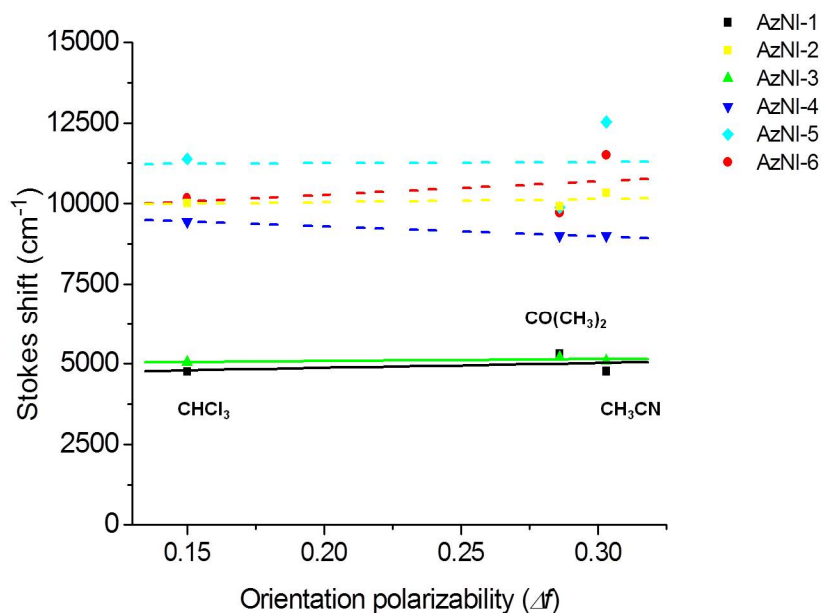


**Figure S10.** Normalized absorption spectra of a thin films and emission spectra in solutions and blends PVK:PBD:AzNI (and selected a thin films) with emission of the matrix.

**Table S5.** Life-time measurements with a time-correlated single photon counting (TCSPC) method.

Code	Medium	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)	$\Sigma\tau$ (ns)	$\chi^2$
AzNI-1	CHCl <sub>3</sub>	3.0	11.0	-	14.01	0.986
AzNI-2		0.2	9.6	-	9.81	1.029
AzNI-3		0.1	9.3	-	9.48	1.159
AzNI-4		0.2	1.1	6.7	8.25	1.028
AzNI-5		0.6	10.3	-	10.89	1.069
AzNI-6		4.4	11.1	-	15.68	1.069

Pulse period = 50 ns. Results were presented as average values of decay after exponential fitting.  
 $\chi^2$ - coefficient of determination.



**Figure S11.** The dependence of the Stokes Shift on solvent orientation polarizability  $\Delta f$ . Stokes shifts calculated according to the equation  $\Delta\nu=(1/\lambda_{\text{abs}}-1/\lambda_{\text{em}})\cdot 10^7$  [cm<sup>-1</sup>].  $\Delta f$  stands for the orientation polarizability defined as:  $\Delta f=[(\epsilon-1)/(2\epsilon-1)]-[(n^2-1)/(2n^2-1)]$ , where  $\epsilon$  and  $n$  are the dielectric constants and the refractive index of the solvent, respectively.

**Table S6.** The electrochemical band gap and the optical band gap.

Molecule	Band gap (eV)	CV method	CHCl <sub>3</sub>	CO(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> CN
AzNI-1	E <sub>g</sub>	1.92 <sup>a</sup>	-	-	-
	E <sub>g</sub> <sup>opt</sup>	2.12 <sup>b</sup>	-	-	-
AzNI-2	E <sub>g</sub>	2.41 <sup>a</sup>	2.61	2.56	2.53
	E <sub>g</sub> <sup>opt</sup>	2.26 <sup>b</sup>	2.99	3.02	3.02
AzNI-3	E <sub>g</sub>	2.14 <sup>a</sup>	-	-	-
	E <sub>g</sub> <sup>opt</sup>	2.36 <sup>b</sup>	2.70	2.73	2.71
AzNI-4	E <sub>g</sub>	1.97 <sup>a</sup>	-	-	-
	E <sub>g</sub> <sup>opt</sup>	1.87 <sup>b</sup>	2.79	2.76	2.76
AzNI-5	E <sub>g</sub>	2.28	-	-	-
	E <sub>g</sub> <sup>opt</sup>	-	3.01	3.04	3.07
AzNI-6	E <sub>g</sub>	2.25 <sup>a</sup>	-	-	-
	E <sub>g</sub> <sup>opt</sup>	2.20 <sup>b</sup>	3.02	3.04	3.06

<sup>a</sup>-DCM, <sup>b</sup>- ACN

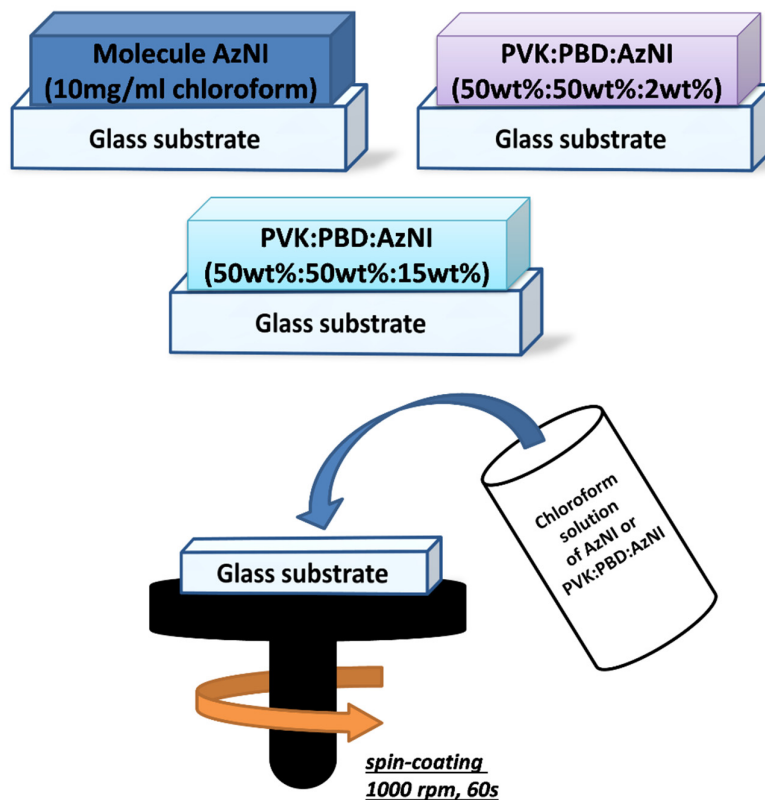


Figure S12. The demonstrative drawing of obtaining thin layers on the glass substrate.

## 7. Optimized geometries of the compounds in ground and excited states

Ground state

AzNI-1

C	-1.578280000	0.552602000	-0.804180000
C	-1.651581000	1.962006000	-0.666734000
C	-0.357180000	-0.085072000	-0.828105000
C	-0.446942000	2.717836000	-0.554673000
C	0.848455000	0.649910000	-0.684600000
C	0.792589000	2.033166000	-0.564916000
C	-2.902421000	2.621866000	-0.649806000
C	-2.963302000	3.998212000	-0.522374000
C	-0.546292000	4.128396000	-0.435131000
C	-1.777288000	4.751841000	-0.416453000
C	-2.819260000	-0.250278000	-0.930123000
C	-4.158293000	1.843551000	-0.765925000
N	-4.028625000	0.458193000	-0.939353000
O	-2.809027000	-1.470457000	-1.024471000
O	-5.264639000	2.365788000	-0.720803000
N	2.051562000	-0.063963000	-0.737225000
C	2.990490000	0.241207000	0.087728000
C	4.324653000	-0.355516000	0.145095000
C	3.731662000	-2.352113000	-1.274956000
C	4.648064000	-1.599766000	-0.477456000
C	4.093085000	-3.553235000	-1.832520000

C	5.963497000	-2.162921000	-0.282573000
C	5.390459000	-4.097151000	-1.641099000
C	6.299795000	-3.414430000	-0.881605000
C	5.313891000	0.336571000	0.910758000
C	6.901242000	-1.484343000	0.497159000
C	6.617818000	-0.254628000	1.091514000
C	5.109692000	1.624154000	1.502863000
C	6.087395000	2.244842000	2.237368000
C	7.610148000	0.420222000	1.865756000
C	7.356015000	1.637238000	2.433723000
H	2.786517000	0.998559000	0.850710000
H	-0.319722000	-1.161766000	-0.944723000
H	1.713301000	2.606465000	-0.515206000
H	-3.937334000	4.473815000	-0.509320000
H	0.366149000	4.712237000	-0.354269000
H	-1.836770000	5.831074000	-0.320644000
H	2.745778000	-1.946494000	-1.443401000
H	3.371388000	-4.097463000	-2.434142000
H	5.652565000	-5.047870000	-2.094418000
H	7.298009000	-3.809489000	-0.716045000
H	7.884892000	-1.924520000	0.640655000
H	4.174896000	2.148833000	1.357831000
H	5.891237000	3.222007000	2.667798000
H	8.577385000	-0.059287000	1.985545000
H	8.115277000	2.144965000	3.019485000
C	-5.268724000	-0.326692000	-1.049354000
H	-5.041602000	-1.193248000	-1.670596000
H	-6.000868000	0.305825000	-1.551680000
C	-5.790174000	-0.768786000	0.317979000
H	-5.015286000	-1.363871000	0.814975000
H	-5.966646000	0.121726000	0.932332000
C	-7.079010000	-1.585175000	0.203461000
H	-6.898080000	-2.465746000	-0.428445000
H	-7.843872000	-0.988829000	-0.313103000
C	-7.622782000	-2.039315000	1.560350000
H	-6.856820000	-2.633821000	2.077608000
H	-7.801662000	-1.158480000	2.192677000
C	-8.912877000	-2.857339000	1.455671000
H	-8.732209000	-3.736562000	0.822926000
H	-9.676403000	-2.262039000	0.937313000
C	-9.448930000	-3.306168000	2.816572000
H	-8.716978000	-3.929689000	3.342120000
H	-9.667659000	-2.444627000	3.457384000
H	-10.370375000	-3.888126000	2.714401000
AzNI-2			
C	-6.097349000	-0.612918000	-0.163552000
C	-6.295074000	0.643606000	-0.798101000
C	-7.246806000	-1.450882000	0.031901000
C	-7.545582000	1.048583000	-1.207063000
C	-8.522640000	-1.001927000	-0.401087000
C	-8.674383000	0.221429000	-1.007392000
C	-4.819808000	-1.092624000	0.288206000
C	-4.725408000	-2.341539000	0.887818000

C	-7.093784000	-2.716397000	0.651232000
C	-5.856513000	-3.154990000	1.068682000
C	-3.604317000	-0.288690000	0.137734000
C	1.013793000	0.334515000	-0.182444000
C	0.997965000	1.697439000	0.208675000
C	-0.122615000	-0.437082000	-0.073780000
C	-0.207552000	2.266189000	0.717044000
C	-1.338972000	0.125138000	0.393732000
C	-1.365818000	1.455205000	0.794630000
C	2.167079000	2.488360000	0.118043000
C	2.146429000	3.812216000	0.519449000
C	-0.191795000	3.626016000	1.122683000
C	0.959073000	4.380766000	1.022285000
C	2.262236000	-0.279130000	-0.697859000
C	3.425885000	1.903061000	-0.401098000
N	3.377116000	0.563112000	-0.810684000
O	2.334405000	-1.457581000	-1.019643000
O	4.467272000	2.541994000	-0.479076000
N	-2.447662000	-0.724965000	0.483423000
H	-3.707804000	0.714277000	-0.290157000
H	-5.453545000	1.302449000	-0.974237000
H	-7.665890000	2.013290000	-1.690108000
H	-9.379574000	-1.650570000	-0.243097000
H	-9.653916000	0.554540000	-1.335072000
H	-3.746758000	-2.674207000	1.215042000
H	-7.974937000	-3.336597000	0.789418000
H	-5.749678000	-4.126385000	1.540500000
H	-0.090642000	-1.481747000	-0.359661000
H	-2.277358000	1.874100000	1.209990000
H	3.059319000	4.391218000	0.438728000
H	-1.104892000	4.066206000	1.513084000
H	0.954650000	5.420025000	1.334312000
C	4.624393000	-0.033742000	-1.314866000
H	5.173088000	0.759797000	-1.822510000
H	4.340134000	-0.803427000	-2.032669000
C	5.467798000	-0.634345000	-0.190182000
H	5.698984000	0.153606000	0.535938000
H	4.873353000	-1.395839000	0.327785000
C	6.764296000	-1.254580000	-0.714631000
H	7.344080000	-0.489838000	-1.249914000
H	6.524107000	-2.030961000	-1.454224000
C	7.628901000	-1.861312000	0.393275000
H	7.867492000	-1.084858000	1.133475000
H	7.048007000	-2.624220000	0.930112000
C	8.928649000	-2.485067000	-0.122487000
H	9.506646000	-1.721584000	-0.660147000
H	8.688009000	-3.260379000	-0.862098000
C	9.786594000	-3.087696000	0.991792000
H	10.067903000	-2.326287000	1.727905000
H	9.243107000	-3.875792000	1.524948000
H	10.708479000	-3.526751000	0.597409000

AzNI-3

C	-2.513761000	0.670540000	-0.831479000
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C	-2.592531000	1.993609000	-0.327307000
C	-1.291120000	0.102902000	-1.116725000
C	-1.392204000	2.735873000	-0.118470000
C	-0.086643000	0.816739000	-0.882666000
C	-0.149557000	2.119939000	-0.403774000
C	-3.845409000	2.584295000	-0.041397000
C	-3.912263000	3.878543000	0.443101000
C	-1.498504000	4.063901000	0.370521000
C	-2.731032000	4.619367000	0.647303000
C	-3.751166000	-0.114196000	-1.063053000
C	-5.097085000	1.820479000	-0.256586000
N	-4.965703000	0.531993000	-0.793325000
O	-3.734666000	-1.268029000	-1.470442000
O	-6.201881000	2.276147000	0.009371000
N	1.113362000	0.176186000	-1.209792000
C	2.130027000	0.308949000	-0.434603000
H	2.032573000	0.857646000	0.508086000
C	3.434990000	-0.260732000	-0.760166000
C	4.545605000	-0.144844000	0.119326000
C	3.584231000	-0.936080000	-1.985364000
C	5.798012000	-0.717716000	-0.273865000
C	4.791679000	-1.491355000	-2.360523000
C	5.918370000	-1.395052000	-1.524293000
C	6.937596000	-0.619026000	0.579361000
C	8.185301000	-1.190089000	0.184383000
C	7.181985000	-1.959464000	-1.895481000
C	8.267423000	-1.861835000	-1.079543000
C	4.486097000	0.518624000	1.393631000
C	5.574812000	0.610760000	2.205629000
C	6.839329000	0.050257000	1.833928000
C	9.291320000	-1.078438000	1.041595000
C	7.970565000	0.137753000	2.659251000
C	9.183531000	-0.421539000	2.264645000
H	-1.247229000	-0.904409000	-1.513537000
H	0.764532000	2.692464000	-0.278990000
H	-4.887560000	4.301416000	0.655466000
H	-0.589730000	4.637766000	0.527888000
H	-2.795575000	5.634877000	1.024185000
H	2.714263000	-1.006933000	-2.627965000
H	4.882728000	-2.008392000	-3.311201000
H	7.254111000	-2.471114000	-2.850718000
H	9.219307000	-2.294389000	-1.373830000
H	3.553541000	0.956064000	1.727285000
H	5.497038000	1.117608000	3.163278000
H	10.238719000	-1.513963000	0.737569000
H	7.888801000	0.648726000	3.614195000
H	10.049660000	-0.345493000	2.914341000
C	-6.201029000	-0.239185000	-1.005754000
H	-6.016269000	-0.908811000	-1.845931000
H	-6.980378000	0.476367000	-1.268556000
C	-6.600612000	-1.035132000	0.236733000
H	-5.779879000	-1.712225000	0.500407000
H	-6.735251000	-0.338996000	1.072710000
C	-7.884981000	-1.836434000	0.015439000

H	-7.747354000	-2.518524000	-0.835006000
H	-8.697168000	-1.152697000	-0.268014000
C	-8.308253000	-2.641700000	1.246472000
H	-7.494954000	-3.323759000	1.531137000
H	-8.444006000	-1.959378000	2.097198000
C	-9.592989000	-3.447149000	1.033939000
H	-9.455383000	-4.127893000	0.183241000
H	-10.403891000	-2.763991000	0.747950000
C	-10.008669000	-4.247839000	2.269632000
H	-9.228167000	-4.960904000	2.557884000
H	-10.183697000	-3.587487000	3.126397000
H	-10.928397000	-4.814136000	2.091885000

## AzNI-4

C	2.300901000	0.702448000	-0.410297000
C	2.686806000	2.013782000	-0.041043000
C	0.967403000	0.354289000	-0.470819000
C	1.679594000	2.981614000	0.252491000
C	-0.046815000	1.301029000	-0.164207000
C	0.321634000	2.599015000	0.166640000
C	4.053525000	2.373093000	0.028277000
C	4.418257000	3.657972000	0.387786000
C	2.090941000	4.292212000	0.613013000
C	3.429246000	4.619684000	0.679929000
C	3.329642000	-0.313022000	-0.739550000
C	5.103322000	1.374586000	-0.281275000
N	4.666079000	0.104442000	-0.686056000
O	3.045979000	-1.465001000	-1.043819000
O	6.298954000	1.625305000	-0.200912000
C	-4.216027000	0.325667000	-0.470781000
C	-5.541101000	-0.058208000	-0.554563000
C	-3.225174000	-0.565733000	-0.022895000
C	-5.946219000	-1.370326000	-0.199348000
C	-3.623930000	-1.860444000	0.337083000
C	-4.949705000	-2.260847000	0.258720000
N	-7.269088000	-1.776725000	-0.307494000
C	-7.658007000	-3.081249000	0.206060000
C	-8.322346000	-0.801619000	-0.504985000
C	-8.621479000	0.021317000	0.775839000
C	-9.670697000	1.011655000	0.548489000
N	-10.507820000	1.783320000	0.322531000
H	0.714973000	-0.651776000	-0.785525000
H	-0.461247000	3.321480000	0.373913000
H	5.473460000	3.901740000	0.436328000
H	1.331028000	5.035176000	0.836971000
H	3.728096000	5.624972000	0.958363000
H	-3.917635000	1.330654000	-0.748362000
H	-6.265406000	0.665131000	-0.906726000
H	-2.878722000	-2.568435000	0.690491000
H	-5.208618000	-3.268498000	0.554570000
H	-8.721202000	-3.233341000	0.016572000
H	-7.110999000	-3.878525000	-0.306823000
H	-7.479708000	-3.185020000	1.286041000
H	-8.064640000	-0.125284000	-1.322985000

H	-9.227071000	-1.328270000	-0.815226000
H	-8.931023000	-0.649642000	1.584354000
H	-7.710244000	0.529837000	1.107098000
C	5.698782000	-0.898037000	-0.992653000
H	6.548006000	-0.359969000	-1.414258000
H	5.277620000	-1.568281000	-1.742226000
C	6.123751000	-1.681652000	0.249233000
H	6.502457000	-0.976340000	0.998031000
H	5.240790000	-2.172205000	0.675250000
C	7.195017000	-2.726026000	-0.070382000
H	8.068760000	-2.229216000	-0.514707000
H	6.814359000	-3.417901000	-0.834693000
C	7.639261000	-3.525315000	1.157918000
H	8.017928000	-2.832037000	1.920506000
H	6.764365000	-4.018305000	1.602010000
C	8.709600000	-4.569944000	0.836049000
H	9.606985000	-4.099047000	0.419411000
H	9.009567000	-5.126700000	1.729446000
H	8.344744000	-5.293658000	0.098607000
N	-1.414335000	1.004238000	-0.224045000
C	-1.827480000	-0.175734000	0.074112000
H	-1.142165000	-0.957133000	0.433828000

## AzNI-5

C	-4.388811000	0.385012000	-0.776528000
C	-5.701826000	0.818661000	-0.865908000
C	-3.948657000	-0.314901000	0.359782000
C	-4.860191000	-0.564874000	1.395498000
C	-6.623822000	0.568689000	0.169116000
C	-6.177314000	-0.131897000	1.301022000
C	-2.570201000	-0.783030000	0.481093000
C	1.987701000	-0.766953000	-0.555710000
C	2.242251000	-2.082763000	-0.092734000
C	0.695337000	-0.300020000	-0.658399000
C	1.146756000	-2.922971000	0.266640000
C	-0.402277000	-1.113153000	-0.273905000
C	-0.169222000	-2.409453000	0.167759000
C	3.566384000	-2.570320000	0.005427000
C	3.804203000	-3.857982000	0.451990000
C	1.426895000	-4.241018000	0.711930000
C	2.726698000	-4.694971000	0.804718000
C	3.113273000	0.118784000	-0.941974000
C	4.710043000	-1.704636000	-0.367720000
N	4.401495000	-0.427420000	-0.856715000
O	2.946890000	1.270414000	-1.320914000
O	5.874184000	-2.069971000	-0.267074000
N	-1.685749000	-0.572565000	-0.422640000
H	-2.326039000	-1.323629000	1.407972000
C	-8.025237000	1.032422000	0.065873000
C	-8.697886000	1.019648000	-1.166694000
C	-8.715193000	1.495637000	1.197790000
C	-10.017370000	1.454516000	-1.263684000
C	-10.034306000	1.931411000	1.100416000
C	-10.691153000	1.912366000	-0.130678000

H	-3.676542000	0.585673000	-1.569118000
H	-6.021669000	1.383606000	-1.735282000
H	-4.532461000	-1.112121000	2.275495000
H	-6.877201000	-0.359351000	2.098090000
H	0.515486000	0.702988000	-1.026755000
H	-1.007998000	-3.055017000	0.409697000
H	4.830465000	-4.200651000	0.519049000
H	0.598286000	-4.888740000	0.983544000
H	2.924981000	-5.704223000	1.150452000
H	-8.189999000	0.639906000	-2.047400000
H	-8.202381000	1.540411000	2.153255000
H	-10.522849000	1.428182000	-2.224168000
H	-10.547217000	2.295045000	1.985548000
H	-11.719308000	2.252094000	-0.206580000
C	5.528678000	0.443939000	-1.225763000
H	5.174310000	1.101514000	-2.019788000
H	6.318211000	-0.203535000	-1.607694000
C	6.034073000	1.262262000	-0.037548000
H	5.206732000	1.867387000	0.350926000
H	6.341666000	0.574426000	0.758603000
C	7.204818000	2.168705000	-0.422865000
H	6.893423000	2.841540000	-1.233895000
H	8.021953000	1.556439000	-0.828951000
C	7.730365000	2.999894000	0.750152000
H	6.912372000	3.610382000	1.157446000
H	8.040071000	2.326854000	1.561826000
C	8.902109000	3.910615000	0.373172000
H	8.590810000	4.581470000	-0.438660000
H	9.717847000	3.298778000	-0.034608000
C	9.420668000	4.737410000	1.551449000
H	8.632809000	5.381663000	1.957585000
H	9.767914000	4.089959000	2.364447000
H	10.256805000	5.379121000	1.256058000

## AzNI-6

C	4.012226000	-1.067948000	-1.413576000
C	5.352025000	-0.713371000	-1.346526000
C	3.122528000	-0.712424000	-0.387921000
C	3.605934000	0.013674000	0.715653000
C	5.838237000	0.013922000	-0.242260000
C	4.940163000	0.372495000	0.788379000
C	1.718417000	-1.101674000	-0.484998000
C	-2.823294000	-0.761185000	0.574394000
C	-3.161203000	-2.075971000	0.164936000
C	-1.504164000	-0.370476000	0.651058000
C	-2.121941000	-2.995054000	-0.167462000
C	-0.461403000	-1.263495000	0.291874000
C	-0.776462000	-2.559512000	-0.096899000
C	-4.513315000	-2.485000000	0.093755000
C	-4.832738000	-3.772138000	-0.300275000
C	-2.485421000	-4.309945000	-0.558656000
C	-3.811164000	-4.686708000	-0.625902000
C	-3.889698000	0.206113000	0.932174000
C	-5.599082000	-1.537025000	0.439007000

N	-5.209400000	-0.263041000	0.875643000
O	-3.650119000	1.359151000	1.264665000
O	-6.784018000	-1.834187000	0.359340000
C	-6.278418000	0.689445000	1.216398000
N	0.853361000	-0.796014000	0.410730000
H	1.437584000	-1.668603000	-1.385175000
C	7.206863000	0.381533000	-0.165264000
C	8.379117000	0.697850000	-0.096917000
C	9.749617000	1.068222000	-0.016529000
C	10.647854000	0.709803000	-1.040581000
C	10.228068000	1.798935000	1.088533000
C	11.987388000	1.074597000	-0.957085000
C	11.569430000	2.159010000	1.162713000
C	12.452633000	1.799096000	0.142495000
C	-6.742979000	1.489814000	-0.000364000
C	-7.852544000	2.481021000	0.356160000
C	-8.337513000	3.295591000	-0.845652000
C	-9.447544000	4.291022000	-0.497111000
C	-9.926493000	5.100142000	-1.704074000
H	3.644150000	-1.627646000	-2.269241000
H	6.037035000	-0.989910000	-2.140165000
H	2.909361000	0.284680000	1.501066000
H	5.313848000	0.933295000	1.638009000
H	-1.260501000	0.633223000	0.978568000
H	0.019277000	-3.264362000	-0.317836000
H	-5.878483000	-4.053735000	-0.347846000
H	-1.700073000	-5.017262000	-0.809305000
H	-4.073445000	-5.694647000	-0.930342000
H	-7.102666000	0.106892000	1.628355000
H	-5.878122000	1.354733000	1.981637000
H	10.279877000	0.147296000	-1.891784000
H	9.536770000	2.075308000	1.877230000
H	12.671402000	0.793477000	-1.751738000
H	11.927956000	2.722246000	2.018614000
H	13.498742000	2.082036000	0.204014000
H	-5.883555000	2.027067000	-0.417881000
H	-7.099146000	0.791372000	-0.766459000
H	-8.701625000	1.936628000	0.792259000
H	-7.493043000	3.165175000	1.137264000
H	-7.487727000	3.837876000	-1.283232000
H	-8.695805000	2.611098000	-1.627190000
H	-10.294946000	3.747309000	-0.058554000
H	-9.087620000	4.973516000	0.284347000
H	-9.104940000	5.678045000	-2.142031000
H	-10.320762000	4.443126000	-2.487411000
H	-10.718910000	5.803286000	-1.428690000

S<sub>1</sub> state in CHCl<sub>3</sub>

AzNI-1

C	-1.560668000	0.584641000	-0.330040000
C	-1.654530000	1.968896000	-0.005354000
C	-0.344173000	-0.057211000	-0.295561000
C	-0.466863000	2.683856000	0.362813000
C	0.855520000	0.638661000	0.034944000

C	0.764620000	2.007254000	0.382117000
C	-2.897879000	2.629922000	-0.024627000
C	-2.984839000	3.978043000	0.315293000
C	-0.595669000	4.061165000	0.705111000
C	-1.826788000	4.687478000	0.679492000
C	-2.773412000	-0.175172000	-0.696687000
C	-4.122920000	1.894203000	-0.397844000
N	-3.974243000	0.544205000	-0.745185000
O	-2.756586000	-1.376165000	-0.955429000
O	-5.233452000	2.419591000	-0.413317000
N	2.005577000	-0.096940000	0.014498000
C	3.191764000	0.482891000	-0.046405000
C	4.433496000	-0.179826000	0.145554000
C	3.452917000	-2.323245000	1.032921000
C	4.531815000	-1.580708000	0.512385000
C	3.568470000	-3.687851000	1.305031000
C	5.789006000	-2.261263000	0.337726000
C	4.781547000	-4.356119000	1.094419000
C	5.874843000	-3.649691000	0.618775000
C	5.659863000	0.561900000	-0.112324000
C	6.923847000	-1.549858000	-0.085149000
C	6.895193000	-0.157437000	-0.276680000
C	5.707741000	1.966352000	-0.220118000
C	6.886545000	2.640514000	-0.535349000
C	8.077972000	0.551346000	-0.609884000
C	8.076750000	1.929876000	-0.744166000
H	3.243056000	1.528911000	-0.352024000
H	-0.283704000	-1.111151000	-0.540321000
H	1.651709000	2.546630000	0.696665000
H	-3.955394000	4.459272000	0.294071000
H	0.295741000	4.613112000	0.987799000
H	-1.904442000	5.737198000	0.943312000
H	2.518805000	-1.815630000	1.224875000
H	2.710298000	-4.227057000	1.692457000
H	4.868364000	-5.416201000	1.308877000
H	6.824163000	-4.151539000	0.456415000
H	7.863725000	-2.080108000	-0.210104000
H	4.821867000	2.557439000	-0.024360000
H	6.878129000	3.722845000	-0.608962000
H	8.994399000	-0.013407000	-0.752962000
H	8.991868000	2.455749000	-0.995010000
C	-5.191980000	-0.198991000	-1.106379000
H	-4.895778000	-0.969493000	-1.818091000
H	-5.863725000	0.507258000	-1.593863000
C	-5.865508000	-0.825899000	0.114408000
H	-5.150472000	-1.494381000	0.607784000
H	-6.114155000	-0.031079000	0.827226000
C	-7.129140000	-1.601791000	-0.262371000
H	-6.872580000	-2.385384000	-0.988676000
H	-7.831816000	-0.928651000	-0.772746000
C	-7.823527000	-2.237934000	0.944406000
H	-7.119475000	-2.908937000	1.456061000
H	-8.079380000	-1.453898000	1.670730000
C	-9.088425000	-3.018055000	0.575586000

H	-8.830455000	-3.800471000	-0.150589000
H	-9.789709000	-2.346192000	0.062892000
C	-9.776301000	-3.649689000	1.787617000
H	-9.106361000	-4.349442000	2.299893000
H	-10.072721000	-2.885102000	2.514556000
H	-10.676334000	-4.201092000	1.497340000
AzNI-2			
C	-6.136089000	-0.585025000	0.105050000
C	-6.490131000	0.772824000	0.244559000
C	-7.187972000	-1.561023000	0.133659000
C	-7.819501000	1.164676000	0.389088000
C	-8.530771000	-1.134625000	0.282490000
C	-8.844810000	0.210247000	0.406936000
C	-4.772540000	-1.037387000	-0.058742000
C	-4.524355000	-2.429898000	-0.168634000
C	-6.877858000	-2.935107000	0.018255000
C	-5.556271000	-3.356885000	-0.128949000
C	-3.664591000	-0.125259000	-0.111437000
C	1.057693000	0.373657000	-0.538125000
C	1.038928000	1.765678000	-0.212411000
C	-0.112844000	-0.365239000	-0.501200000
C	-0.206335000	2.390580000	0.155950000
C	-1.347995000	0.235959000	-0.170951000
C	-1.377040000	1.620017000	0.173259000
C	2.224246000	2.523299000	-0.234242000
C	2.203007000	3.886442000	0.106612000
C	-0.186098000	3.776758000	0.493460000
C	0.997774000	4.498656000	0.467022000
C	2.315430000	-0.283199000	-0.905482000
C	3.495779000	1.891868000	-0.606490000
N	3.454670000	0.532717000	-0.950544000
O	2.398446000	-1.486564000	-1.171814000
O	4.566718000	2.505531000	-0.628592000
N	-2.438611000	-0.592671000	-0.212366000
H	-3.868386000	0.943713000	-0.099036000
H	-5.725512000	1.539136000	0.249541000
H	-8.056236000	2.218065000	0.491047000
H	-9.315911000	-1.883981000	0.297448000
H	-9.877575000	0.520775000	0.519997000
H	-3.495675000	-2.742833000	-0.295773000
H	-7.685209000	-3.660203000	0.043611000
H	-5.334634000	-4.414583000	-0.220906000
H	-0.091926000	-1.419654000	-0.748347000
H	-2.303063000	2.091909000	0.480899000
H	3.134390000	4.439191000	0.083223000
H	-1.118291000	4.257891000	0.773825000
H	0.990447000	5.552186000	0.729171000
C	4.725648000	-0.106492000	-1.318505000
H	5.333180000	0.651652000	-1.812601000
H	4.489850000	-0.903534000	-2.023666000
C	5.460569000	-0.669887000	-0.101803000
H	5.641012000	0.144832000	0.609062000
H	4.810800000	-1.399227000	0.395768000

C	6.786863000	-1.329573000	-0.484325000
H	7.423773000	-0.596262000	-0.998308000
H	6.598751000	-2.133580000	-1.209427000
C	7.542006000	-1.899846000	0.718869000
H	7.727850000	-1.095793000	1.444651000
H	6.904564000	-2.632590000	1.233243000
C	8.871754000	-2.560619000	0.344999000
H	9.506603000	-1.827055000	-0.169752000
H	8.684106000	-3.363137000	-0.380870000
C	9.619301000	-3.126963000	1.554007000
H	9.846519000	-2.338667000	2.280562000
H	9.018378000	-3.885613000	2.068096000
H	10.565347000	-3.593056000	1.260353000

## AzNI-3

C	-2.515426000	0.589860000	-0.407497000
C	-2.611601000	1.880403000	0.193607000
C	-1.274552000	0.000668000	-0.592897000
C	-1.409252000	2.560033000	0.598336000
C	-0.085265000	0.644877000	-0.189652000
C	-0.167219000	1.933853000	0.399255000
C	-3.866002000	2.491068000	0.391381000
C	-3.952710000	3.760370000	0.981229000
C	-1.539714000	3.851228000	1.187327000
C	-2.786507000	4.429428000	1.370948000
C	-3.724793000	-0.121586000	-0.830012000
C	-5.093848000	1.797316000	-0.016765000
N	-4.942204000	0.548020000	-0.636410000
O	-3.709309000	-1.248756000	-1.334926000
O	-6.221370000	2.267799000	0.159495000
N	1.072675000	-0.067549000	-0.418349000
C	2.237454000	0.352563000	0.006199000
H	2.340954000	1.262406000	0.594846000
C	3.425206000	-0.412285000	-0.284716000
C	4.737849000	0.009988000	0.148104000
C	3.306133000	-1.620106000	-1.018848000
C	5.868766000	-0.802886000	-0.164742000
C	4.401739000	-2.393451000	-1.316113000
C	5.709289000	-2.014923000	-0.901305000
C	7.170712000	-0.413136000	0.253871000
C	8.300713000	-1.227396000	-0.057654000
C	6.844403000	-2.807101000	-1.200430000
C	8.105556000	-2.429580000	-0.792508000
C	4.957988000	1.209529000	0.876209000
C	6.220386000	1.589356000	1.283341000
C	7.356378000	0.794188000	0.987970000
C	9.582817000	-0.815539000	0.372896000
C	8.661573000	1.165660000	1.397793000
C	9.756387000	0.366846000	1.091598000
H	-1.208602000	-0.980238000	-1.048134000
H	0.729006000	2.469614000	0.690724000
H	-4.932035000	4.201916000	1.120753000
H	-0.640037000	4.376757000	1.493594000
H	-2.860479000	5.413772000	1.823256000

H	2.312875000	-1.913145000	-1.334126000
H	4.280710000	-3.315467000	-1.876387000
H	6.705207000	-3.725679000	-1.761594000
H	8.966351000	-3.046775000	-1.028488000
H	4.125113000	1.854639000	1.122756000
H	6.353812000	2.511983000	1.838807000
H	10.439615000	-1.437749000	0.134002000
H	8.793260000	2.086899000	1.956354000
H	10.749355000	0.662991000	1.411297000
C	-6.166834000	-0.152448000	-1.046606000
H	-5.913214000	-0.756203000	-1.918028000
H	-6.892790000	0.610250000	-1.328420000
C	-6.726030000	-1.035060000	0.069556000
H	-5.959471000	-1.762946000	0.359831000
H	-6.928990000	-0.407849000	0.945443000
C	-8.001770000	-1.764181000	-0.356226000
H	-7.792297000	-2.377022000	-1.244042000
H	-8.757293000	-1.027839000	-0.663794000
C	-8.581863000	-2.653274000	0.746553000
H	-7.825312000	-3.388052000	1.055708000
H	-8.790986000	-2.040138000	1.634320000
C	-9.858339000	-3.387770000	0.327296000
H	-9.647327000	-3.999588000	-0.560006000
H	-10.612317000	-2.651926000	0.017163000
C	-10.431351000	-4.272864000	1.436149000
H	-9.708179000	-5.037036000	1.742793000
H	-10.680346000	-3.679975000	2.323512000
H	-11.342088000	-4.786301000	1.111411000

## AzNI-4

C	2.328440000	0.572652000	-0.420177000
C	2.683042000	1.913038000	-0.091837000
C	0.982818000	0.175127000	-0.448634000
C	1.650585000	2.876205000	0.188798000
C	-0.019561000	1.114532000	-0.169690000
C	0.304806000	2.450123000	0.116037000
C	4.042231000	2.312850000	-0.045394000
C	4.373020000	3.646160000	0.284781000
C	2.024758000	4.204584000	0.510816000
C	3.371607000	4.572038000	0.555099000
C	3.363864000	-0.403105000	-0.722331000
C	5.096424000	1.355179000	-0.330090000
N	4.686708000	0.057650000	-0.684504000
O	3.120484000	-1.593034000	-1.002318000
O	6.309441000	1.630164000	-0.279178000
C	-4.194468000	0.343431000	-0.248862000
C	-5.533930000	0.058924000	-0.294593000
C	-3.233197000	-0.681860000	-0.053453000
C	-5.996532000	-1.289256000	-0.147341000
C	-3.685844000	-2.013797000	0.093005000
C	-5.024647000	-2.319712000	0.050500000
N	-7.316800000	-1.595608000	-0.187293000
C	-7.785688000	-2.960584000	0.074395000
C	-8.343458000	-0.582775000	-0.425356000

C	-8.792195000	0.072845000	0.901542000
C	-9.840124000	1.064252000	0.668925000
N	-10.670368000	1.846691000	0.458467000
H	0.760605000	-0.846191000	-0.728497000
H	-0.501621000	3.149443000	0.309802000
H	5.421043000	3.919317000	0.316441000
H	1.246921000	4.931980000	0.722001000
H	3.639217000	5.594743000	0.804649000
H	-3.840437000	1.361128000	-0.355617000
H	-6.234859000	0.870160000	-0.431663000
H	-2.960539000	-2.806974000	0.238194000
H	-5.336088000	-3.348707000	0.157619000
H	-8.872662000	-2.955783000	0.109139000
H	-7.464077000	-3.635642000	-0.723375000
H	-7.405738000	-3.323104000	1.031653000
H	-7.972239000	0.167245000	-1.121541000
H	-9.190765000	-1.073063000	-0.904258000
H	-9.172007000	-0.688579000	1.589992000
H	-7.942799000	0.560398000	1.390090000
C	5.741791000	-0.918083000	-0.975717000
H	6.571070000	-0.370417000	-1.423917000
H	5.332982000	-1.626758000	-1.696348000
C	6.209957000	-1.650756000	0.282230000
H	6.572912000	-0.909040000	1.003152000
H	5.347615000	-2.153358000	0.736084000
C	7.310684000	-2.670700000	-0.013771000
H	8.164099000	-2.161424000	-0.483265000
H	6.945966000	-3.399071000	-0.751899000
C	7.792816000	-3.415727000	1.234244000
H	8.155168000	-2.686188000	1.970619000
H	6.938702000	-3.922669000	1.702804000
C	8.894479000	-4.434802000	0.936126000
H	9.771947000	-3.947847000	0.495822000
H	9.220666000	-4.952607000	1.843975000
H	8.547212000	-5.193256000	0.225297000
N	-1.394306000	0.820948000	-0.156715000
C	-1.813221000	-0.389059000	-0.007771000
H	-1.142983000	-1.237079000	0.162414000

## AzNI-5

C	3.977208000	-0.896304000	0.458161000
C	5.154208000	-0.697921000	-0.234113000
C	3.880470000	-0.575343000	1.847539000
C	5.052863000	-0.057085000	2.479234000
C	6.307747000	-0.176065000	0.392469000
C	6.218479000	0.134466000	1.770257000
C	2.692009000	-0.730935000	2.569731000
C	-1.566927000	-0.544322000	0.358071000
C	-1.462860000	0.868812000	0.152539000
C	-0.572085000	-1.232188000	0.986970000
C	-0.299892000	1.566432000	0.612522000
C	0.619045000	-0.560580000	1.468366000
C	0.717705000	0.850868000	1.259701000
C	-2.490480000	1.573165000	-0.493758000

C	-2.385412000	2.947455000	-0.688699000
C	-0.223224000	2.970646000	0.392757000
C	-1.246984000	3.642958000	-0.244258000
C	-2.772104000	-1.275051000	-0.115420000
C	-3.700444000	0.863490000	-0.972678000
N	-3.743759000	-0.523304000	-0.783173000
O	-2.921464000	-2.477652000	0.059341000
O	-4.630404000	1.447309000	-1.516365000
N	1.538361000	-1.310989000	2.055940000
H	2.675590000	-0.494026000	3.632758000
C	7.558340000	0.033157000	-0.359098000
C	7.536437000	0.367004000	-1.726293000
C	8.812364000	-0.095197000	0.267091000
C	8.718022000	0.562263000	-2.436955000
C	9.993498000	0.102627000	-0.443664000
C	9.953888000	0.432057000	-1.800082000
H	3.114663000	-1.317513000	-0.045448000
H	5.202778000	-0.979608000	-1.281052000
H	5.009292000	0.202193000	3.533013000
H	7.079854000	0.559691000	2.274904000
H	-0.655831000	-2.301226000	1.139821000
H	1.605942000	1.368410000	1.601750000
H	-3.196341000	3.463319000	-1.188900000
H	0.656621000	3.504312000	0.737191000
H	-1.177162000	4.713010000	-0.404759000
H	6.583694000	0.501171000	-2.227975000
H	8.860488000	-0.381111000	1.312699000
H	8.673407000	0.826716000	-3.489167000
H	10.948257000	-0.011047000	0.060908000
H	10.874684000	0.585127000	-2.353983000
C	-4.949039000	-1.232935000	-1.247358000
H	-4.638309000	-2.241033000	-1.520573000
H	-5.303396000	-0.709810000	-2.135203000
C	-6.037799000	-1.274725000	-0.175180000
H	-5.637132000	-1.767578000	0.718176000
H	-6.295712000	-0.247446000	0.107279000
C	-7.288980000	-2.010970000	-0.658494000
H	-7.018683000	-3.034050000	-0.953949000
H	-7.673370000	-1.521088000	-1.563694000
C	-8.395651000	-2.064091000	0.397755000
H	-8.009774000	-2.552680000	1.303283000
H	-8.663474000	-1.040398000	0.694411000
C	-9.652680000	-2.798422000	-0.076777000
H	-9.382659000	-3.820685000	-0.373446000
H	-10.035524000	-2.309484000	-0.982521000
C	-10.753414000	-2.846041000	0.984930000
H	-10.405905000	-3.358067000	1.889306000
H	-11.063145000	-1.836038000	1.276190000
H	-11.639977000	-3.375310000	0.621441000
AzNI-6			
C	4.275762000	-1.897982000	-0.887036000
C	5.563635000	-1.428064000	-0.798486000
C	3.179658000	-1.131542000	-0.397809000

C	3.446870000	0.142286000	0.189055000
C	5.827092000	-0.154020000	-0.210165000
C	4.730593000	0.617235000	0.280543000
C	1.847291000	-1.641967000	-0.494682000
C	-2.787587000	-0.839698000	0.355490000
C	-3.199787000	-2.139230000	-0.071357000
C	-1.449635000	-0.499714000	0.349679000
C	-2.205526000	-3.086657000	-0.501778000
C	-0.452421000	-1.412601000	-0.078349000
C	-0.853933000	-2.714102000	-0.496032000
C	-4.559995000	-2.496179000	-0.073944000
C	-4.958577000	-3.772082000	-0.494650000
C	-2.651001000	-4.377307000	-0.917430000
C	-3.996774000	-4.702840000	-0.911006000
C	-3.783729000	0.144968000	0.800332000
C	-5.577787000	-1.527360000	0.362779000
N	-5.120248000	-0.278046000	0.805713000
O	-3.490963000	1.287627000	1.158102000
O	-6.784165000	-1.777583000	0.354228000
C	-6.133361000	0.696276000	1.236731000
N	0.829586000	-0.936035000	-0.042880000
H	1.730741000	-2.621093000	-0.965727000
C	7.131332000	0.328573000	-0.120292000
C	8.281033000	0.756801000	-0.040430000
C	9.589818000	1.248381000	0.052311000
C	10.680869000	0.484569000	-0.438287000
C	9.839190000	2.517065000	0.637952000
C	11.971794000	0.979580000	-0.342627000
C	11.136392000	2.996909000	0.725490000
C	12.205113000	2.233476000	0.237464000
C	-6.643494000	1.546921000	0.073200000
C	-7.694721000	2.564404000	0.520590000
C	-8.220312000	3.427571000	-0.629179000
C	-9.273267000	4.449124000	-0.190688000
C	-9.792596000	5.306618000	-1.346667000
H	4.081176000	-2.867488000	-1.335153000
H	6.395539000	-2.014124000	-1.172420000
H	2.606413000	0.718240000	0.556176000
H	4.932092000	1.585499000	0.725142000
H	-1.144179000	0.488508000	0.672091000
H	-0.117604000	-3.445700000	-0.808031000
H	-6.014176000	-4.015492000	-0.486525000
H	-1.911324000	-5.102944000	-1.242189000
H	-4.312865000	-5.690364000	-1.232446000
H	-6.950979000	0.130725000	1.683535000
H	-5.667735000	1.326384000	1.994464000
H	10.487364000	-0.484019000	-0.885138000
H	9.003720000	3.098113000	1.011659000
H	12.803482000	0.393324000	-0.718600000
H	11.323442000	3.966944000	1.173565000
H	13.218249000	2.615121000	0.309047000
H	-5.792576000	2.065990000	-0.383049000
H	-7.067702000	0.883174000	-0.689126000
H	-8.535283000	2.036900000	0.992475000

H	-7.266320000	3.214242000	1.296280000
H	-7.379049000	3.953611000	-1.101776000
H	-8.647028000	2.777055000	-1.405393000
H	-10.112360000	3.921550000	0.282254000
H	-8.845236000	5.097629000	0.585417000
H	-8.977601000	5.868521000	-1.816764000
H	-10.253703000	4.684255000	-2.121883000
H	-10.543062000	6.027850000	-1.007434000

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AzNI-1			
C	-1.564685000	0.502986000	-0.611952000
C	-1.671326000	1.916927000	-0.509777000
C	-0.333245000	-0.105722000	-0.563236000
C	-0.490256000	2.702272000	-0.353264000
C	0.858802000	0.655716000	-0.378015000
C	0.762907000	2.050504000	-0.285479000
C	-2.932005000	2.549538000	-0.570150000
C	-3.024519000	3.929670000	-0.475232000
C	-0.620656000	4.113292000	-0.266824000
C	-1.863455000	4.711822000	-0.324497000
C	-2.783340000	-0.324351000	-0.779626000
C	-4.162966000	1.743680000	-0.734181000
N	-4.002630000	0.358198000	-0.864138000
O	-2.746308000	-1.547664000	-0.845578000
O	-5.281175000	2.246203000	-0.762459000
N	2.035666000	-0.064108000	-0.357738000
C	3.145063000	0.480422000	0.172778000
C	4.391041000	-0.114407000	0.059998000
C	3.940570000	-1.849601000	-1.729504000
C	4.630511000	-1.425054000	-0.600708000
C	4.145424000	-3.141521000	-2.255754000
C	5.601824000	-2.273385000	-0.002624000
C	5.048142000	-3.994126000	-1.641662000
C	5.778132000	-3.559047000	-0.521675000
C	5.559407000	0.521075000	0.731718000
C	6.417766000	-1.770487000	1.089821000
C	6.518810000	-0.341644000	1.324375000
C	5.701537000	1.897708000	0.839407000
C	6.760735000	2.458876000	1.583306000
C	7.550790000	0.225276000	2.077926000
C	7.666514000	1.620351000	2.212670000
H	3.087072000	1.406748000	0.747377000
H	-0.255682000	-1.182562000	-0.653374000
H	1.657443000	2.656208000	-0.192554000
H	-4.004833000	4.389485000	-0.522030000
H	0.274702000	4.716012000	-0.150488000
H	-1.950721000	5.790501000	-0.254320000
H	3.226099000	-1.184918000	-2.196716000
H	3.583315000	-3.462842000	-3.126315000
H	5.203564000	-4.997915000	-2.025452000
H	6.496431000	-4.224746000	-0.051548000

H	7.144063000	-2.432243000	1.550708000
H	4.989856000	2.552441000	0.346057000
H	6.851158000	3.536729000	1.666103000
H	8.272140000	-0.426763000	2.562063000
H	8.477303000	2.035281000	2.803664000
C	-5.223241000	-0.452121000	-1.017186000
H	-4.950254000	-1.331060000	-1.600751000
H	-5.936191000	0.150073000	-1.580017000
C	-5.811904000	-0.862148000	0.332730000
H	-5.057720000	-1.429656000	0.890200000
H	-6.032927000	0.042198000	0.911417000
C	-7.081880000	-1.700455000	0.173404000
H	-6.855258000	-2.597162000	-0.419637000
H	-7.824502000	-1.131018000	-0.402342000
C	-7.692690000	-2.119671000	1.512953000
H	-6.949386000	-2.688750000	2.088507000
H	-7.915550000	-1.222107000	2.106596000
C	-8.966253000	-2.956556000	1.364080000
H	-8.741552000	-3.852691000	0.770420000
H	-9.706650000	-2.386672000	0.786946000
C	-9.570459000	-3.369442000	2.707808000
H	-8.861071000	-3.967200000	3.291152000
H	-9.832834000	-2.490805000	3.307841000
H	-10.478666000	-3.965741000	2.574109000

## AzNI-2

C	-6.113948000	-0.715579000	0.004115000
C	-6.483607000	0.619644000	0.248442000
C	-7.142703000	-1.707670000	-0.015645000
C	-7.809279000	0.979849000	0.465375000
C	-8.481594000	-1.319353000	0.207222000
C	-8.815478000	0.005143000	0.444759000
C	-4.723263000	-1.128909000	-0.230141000
C	-4.467482000	-2.526602000	-0.468411000
C	-6.813918000	-3.079805000	-0.259098000
C	-5.490595000	-3.460857000	-0.479378000
C	-3.667671000	-0.222498000	-0.226544000
C	1.091364000	0.313782000	-0.716243000
C	1.046910000	1.726373000	-0.451312000
C	-0.052600000	-0.432748000	-0.702329000
C	-0.207971000	2.351804000	-0.169743000
C	-1.338833000	0.155674000	-0.432293000
C	-1.383582000	1.571042000	-0.163241000
C	2.221324000	2.487708000	-0.462806000
C	2.177658000	3.862195000	-0.196097000
C	-0.220355000	3.745797000	0.094006000
C	0.955208000	4.483845000	0.080245000
C	2.386806000	-0.344942000	-1.003953000
C	3.524954000	1.849727000	-0.753556000
N	3.516963000	0.479263000	-1.041180000
O	2.485687000	-1.550179000	-1.207648000
O	4.577686000	2.479381000	-0.751579000
N	-2.376607000	-0.682130000	-0.457078000
H	-3.857054000	0.830659000	-0.052790000

H	-5.728870000	1.397023000	0.271821000
H	-8.060243000	2.019212000	0.650883000
H	-9.253557000	-2.083291000	0.189309000
H	-9.850454000	0.284843000	0.613942000
H	-3.440952000	-2.821477000	-0.640546000
H	-7.612624000	-3.814457000	-0.269019000
H	-5.256653000	-4.505179000	-0.663215000
H	-0.010930000	-1.496953000	-0.900948000
H	-2.323825000	2.061176000	0.053484000
H	3.104937000	4.422253000	-0.210329000
H	-1.168442000	4.229122000	0.308733000
H	0.927381000	5.548583000	0.284969000
C	4.812787000	-0.161619000	-1.323830000
H	5.433973000	0.583296000	-1.820548000
H	4.616603000	-0.985795000	-2.009413000
C	5.492902000	-0.669160000	-0.052347000
H	5.637816000	0.174248000	0.632756000
H	4.826061000	-1.382672000	0.445317000
C	6.838028000	-1.334867000	-0.350065000
H	7.493797000	-0.618291000	-0.863589000
H	6.685323000	-2.167728000	-1.050195000
C	7.540097000	-1.852844000	0.907676000
H	7.691105000	-1.019674000	1.608186000
H	6.882680000	-2.567790000	1.421757000
C	8.887012000	-2.521455000	0.618890000
H	9.541820000	-1.805680000	0.104184000
H	8.733811000	-3.352678000	-0.082241000
C	9.581552000	-3.036412000	1.881244000
H	9.774240000	-2.219248000	2.585505000
H	8.960641000	-3.777169000	2.397572000
H	10.540871000	-3.509255000	1.647968000

## AzNI-3

C	-2.506263000	0.536020000	-0.293383000
C	-2.594376000	1.815591000	0.335542000
C	-1.288228000	-0.071351000	-0.462656000
C	-1.400027000	2.458822000	0.786210000
C	-0.070970000	0.547280000	-0.031247000
C	-0.156405000	1.818751000	0.596061000
C	-3.840607000	2.439822000	0.518919000
C	-3.919626000	3.684896000	1.140457000
C	-1.515732000	3.727792000	1.413261000
C	-2.752401000	4.325449000	1.584944000
C	-3.733959000	-0.144947000	-0.762963000
C	-5.080728000	1.777923000	0.057361000
N	-4.941268000	0.542812000	-0.588568000
O	-3.719247000	-1.254515000	-1.285876000
O	-6.191555000	2.273410000	0.219207000
N	1.059756000	-0.167005000	-0.269326000
C	2.279229000	0.320358000	0.053395000
H	2.387309000	1.309959000	0.490241000
C	3.427136000	-0.443174000	-0.182596000
C	4.778853000	0.039461000	0.143307000
C	3.301368000	-1.754997000	-0.768180000

C	5.901814000	-0.795431000	-0.137556000
C	4.386197000	-2.532251000	-1.024335000
C	5.723708000	-2.089965000	-0.724415000
C	7.220861000	-0.348732000	0.164608000
C	8.349243000	-1.184810000	-0.118065000
C	6.842475000	-2.891603000	-0.991975000
C	8.130104000	-2.457611000	-0.699399000
C	5.016068000	1.299539000	0.724573000
C	6.298028000	1.740749000	1.021845000
C	7.426686000	0.936739000	0.751610000
C	9.649616000	-0.712559000	0.192757000
C	8.752734000	1.365028000	1.044903000
C	9.838648000	0.546092000	0.765806000
H	-1.228248000	-1.043441000	-0.937215000
H	0.734690000	2.323226000	0.949812000
H	-4.894338000	4.140314000	1.269513000
H	-0.613932000	4.224381000	1.758107000
H	-2.822979000	5.294884000	2.066354000
H	2.300468000	-2.096459000	-0.998641000
H	4.260256000	-3.515993000	-1.467698000
H	6.689814000	-3.870440000	-1.437379000
H	8.983575000	-3.092952000	-0.914413000
H	4.185705000	1.956345000	0.954064000
H	6.441817000	2.719152000	1.469808000
H	10.502305000	-1.348955000	-0.023156000
H	8.899428000	2.343974000	1.490583000
H	10.843688000	0.886099000	0.994714000
C	-6.171384000	-0.125385000	-1.045531000
H	-5.907406000	-0.709339000	-1.927081000
H	-6.873717000	0.658912000	-1.326905000
C	-6.772535000	-1.024541000	0.034762000
H	-6.027204000	-1.773375000	0.326667000
H	-6.988806000	-0.416848000	0.921121000
C	-8.048707000	-1.719883000	-0.443730000
H	-7.825497000	-2.314067000	-1.340583000
H	-8.782949000	-0.962809000	-0.751952000
C	-8.671799000	-2.625476000	0.621537000
H	-7.935953000	-3.380568000	0.931393000
H	-8.894097000	-2.030712000	1.518496000
C	-9.948732000	-3.327005000	0.150473000
H	-9.724360000	-3.920183000	-0.746076000
H	-10.681849000	-2.570740000	-0.160401000
C	-10.565110000	-4.229210000	1.221564000
H	-9.863165000	-5.013246000	1.527222000
H	-10.827544000	-3.654347000	2.116851000
H	-11.475318000	-4.718389000	0.860257000
AzNI-4			
C	2.312991000	0.540247000	-0.432228000
C	2.675249000	1.886782000	-0.202230000
C	0.970969000	0.143062000	-0.433168000
C	1.652725000	2.867849000	0.032288000
C	-0.051806000	1.103681000	-0.200641000
C	0.312351000	2.449085000	0.022966000

C	4.033622000	2.291763000	-0.193286000
C	4.360678000	3.633051000	0.043861000
C	2.026320000	4.217257000	0.264335000
C	3.365247000	4.590161000	0.268989000
C	3.360126000	-0.458982000	-0.666220000
C	5.097914000	1.313391000	-0.423982000
N	4.687515000	-0.001040000	-0.677738000
O	3.114109000	-1.656035000	-0.851527000
O	6.299669000	1.605339000	-0.404407000
C	-4.220017000	0.396723000	-0.163911000
C	-5.563516000	0.126079000	-0.172231000
C	-3.246272000	-0.644823000	-0.320384000
C	-6.049948000	-1.207163000	-0.339363000
C	-3.740653000	-1.977948000	-0.480652000
C	-5.083610000	-2.251609000	-0.488701000
N	-7.391408000	-1.492520000	-0.362384000
C	-7.852886000	-2.878009000	-0.417517000
C	-8.390069000	-0.464129000	-0.123014000
C	-8.583768000	-0.196350000	1.391267000
C	-9.584078000	0.841588000	1.627349000
N	-10.383429000	1.669409000	1.779278000
H	0.754803000	-0.898880000	-0.619217000
H	-0.487216000	3.162208000	0.195213000
H	5.409802000	3.906751000	0.046619000
H	1.247279000	4.952852000	0.439399000
H	3.641448000	5.623487000	0.448078000
H	-3.863184000	1.410862000	-0.034782000
H	-6.255214000	0.948662000	-0.045653000
H	-3.028984000	-2.789486000	-0.598174000
H	-5.408807000	-3.275799000	-0.612186000
H	-8.941540000	-2.886590000	-0.403361000
H	-7.519653000	-3.363682000	-1.339389000
H	-7.489432000	-3.458679000	0.437144000
H	-8.111058000	0.457975000	-0.634346000
H	-9.333376000	-0.793868000	-0.559708000
H	-8.900206000	-1.114423000	1.896489000
H	-7.635746000	0.114665000	1.841211000
C	5.740565000	-1.001632000	-0.901445000
H	6.568434000	-0.489617000	-1.392027000
H	5.327934000	-1.756340000	-1.570942000
C	6.208431000	-1.643553000	0.405033000
H	6.572180000	-0.854645000	1.073840000
H	5.347541000	-2.114625000	0.893751000
C	7.309313000	-2.680905000	0.176729000
H	8.161469000	-2.204472000	-0.327850000
H	6.943014000	-3.457898000	-0.508804000
C	7.793045000	-3.338182000	1.472523000
H	8.156514000	-2.559896000	2.156520000
H	6.939817000	-3.812151000	1.975619000
C	8.894371000	-4.374901000	1.242056000
H	9.771013000	-3.919013000	0.768221000
H	9.221801000	-4.829348000	2.182619000
H	8.545798000	-5.180015000	0.585401000
N	-1.408527000	0.876721000	-0.165857000

C	-1.863365000	-0.382964000	-0.320412000
H	-1.193358000	-1.234286000	-0.439754000
AzNI-5			
C	-4.207828000	0.643579000	-0.227896000
C	-5.464694000	1.200933000	-0.329918000
C	-4.031087000	-0.666058000	0.312102000
C	-5.198724000	-1.364612000	0.738958000
C	-6.622432000	0.506199000	0.096382000
C	-6.448518000	-0.793000000	0.634481000
C	-2.758692000	-1.267263000	0.428663000
C	1.957309000	-0.792400000	-0.309168000
C	2.261306000	-2.107651000	0.202936000
C	0.666381000	-0.338247000	-0.349050000
C	1.198706000	-2.946008000	0.672031000
C	-0.430311000	-1.140443000	0.106975000
C	-0.127337000	-2.471624000	0.623795000
C	3.579001000	-2.560885000	0.245736000
C	3.879751000	-3.844623000	0.750173000
C	1.529795000	-4.232017000	1.170341000
C	2.853906000	-4.668266000	1.205738000
C	3.047569000	0.080822000	-0.794095000
C	4.683368000	-1.702138000	-0.232233000
N	4.342015000	-0.449292000	-0.754850000
O	2.849916000	1.216089000	-1.217843000
O	5.857230000	-2.058827000	-0.184403000
N	-1.638960000	-0.591634000	0.017111000
H	-2.708607000	-2.269069000	0.852813000
C	-7.960448000	1.111045000	-0.015103000
C	-8.260790000	2.021472000	-1.046437000
C	-8.977821000	0.796294000	0.906112000
C	-9.526098000	2.592163000	-1.151971000
C	-10.242245000	1.368928000	0.800184000
C	-10.523886000	2.269654000	-0.229392000
H	-3.328360000	1.190638000	-0.545067000
H	-5.565589000	2.208896000	-0.718419000
H	-5.093078000	-2.367753000	1.142165000
H	-7.319633000	-1.361531000	0.942038000
H	0.450609000	0.651446000	-0.733146000
H	-0.920583000	-3.115918000	0.979110000
H	4.914950000	-4.162403000	0.769808000
H	0.731907000	-4.876044000	1.526688000
H	3.084843000	-5.655474000	1.591400000
H	-7.504861000	2.259501000	-1.787246000
H	-8.765680000	0.120987000	1.728279000
H	-9.736716000	3.283997000	-1.961705000
H	-11.007448000	1.118380000	1.528463000
H	-11.510089000	2.715349000	-0.311893000
C	5.440133000	0.411767000	-1.225513000
H	5.039800000	1.023165000	-2.034062000
H	6.215083000	-0.246403000	-1.617655000
C	5.997144000	1.294669000	-0.108701000
H	5.185241000	1.912234000	0.292424000
H	6.351983000	0.653189000	0.706383000

C	7.136700000	2.189255000	-0.600879000
H	6.777008000	2.814684000	-1.429518000
H	7.939204000	1.563162000	-1.014712000
C	7.710180000	3.086625000	0.498687000
H	6.906567000	3.711306000	0.912970000
H	8.067948000	2.460835000	1.328192000
C	8.851208000	3.985670000	0.014561000
H	8.491900000	4.608633000	-0.815383000
H	9.652738000	3.359490000	-0.399549000
C	9.417611000	4.879899000	1.119396000
H	8.643019000	5.538325000	1.528463000
H	9.811764000	4.280285000	1.947635000
H	10.230807000	5.511675000	0.748087000

## AzNI-6

C	4.304800000	-1.991759000	-0.658721000
C	5.586044000	-1.507706000	-0.597497000
C	3.183964000	-1.183139000	-0.272665000
C	3.452044000	0.153419000	0.181592000
C	5.843816000	-0.177161000	-0.145684000
C	4.735332000	0.633835000	0.240722000
C	1.882806000	-1.698033000	-0.345842000
C	-2.790820000	-0.825626000	0.344247000
C	-3.195136000	-2.124024000	-0.128766000
C	-1.469496000	-0.474810000	0.373957000
C	-2.201447000	-3.054226000	-0.571108000
C	-0.437216000	-1.377802000	-0.054755000
C	-0.841629000	-2.683388000	-0.531629000
C	-4.547163000	-2.476149000	-0.162446000
C	-4.942412000	-3.740091000	-0.631148000
C	-2.630767000	-4.324106000	-1.036323000
C	-3.980703000	-4.655685000	-1.063838000
C	-3.810782000	0.145922000	0.800087000
C	-5.581674000	-1.520824000	0.291508000
N	-5.142300000	-0.283517000	0.777513000
O	-3.524692000	1.274733000	1.186239000
O	-6.779265000	-1.785594000	0.254805000
C	-6.170152000	0.674075000	1.220128000
N	0.812271000	-0.918190000	0.027464000
H	1.758026000	-2.720501000	-0.699085000
C	7.154719000	0.317778000	-0.084068000
C	8.298335000	0.748955000	-0.031029000
C	9.621965000	1.249483000	0.030131000
C	10.713617000	0.436712000	-0.345724000
C	9.869674000	2.568947000	0.467500000
C	12.010513000	0.933845000	-0.284043000
C	11.171078000	3.054747000	0.524659000
C	12.245046000	2.241844000	0.150211000
C	-6.667370000	1.552781000	0.072324000
C	-7.734265000	2.547950000	0.533142000
C	-8.249120000	3.439246000	-0.599905000
C	-9.318133000	4.438183000	-0.148374000
C	-9.827251000	5.324162000	-1.287229000
H	4.122779000	-3.005113000	-1.004579000

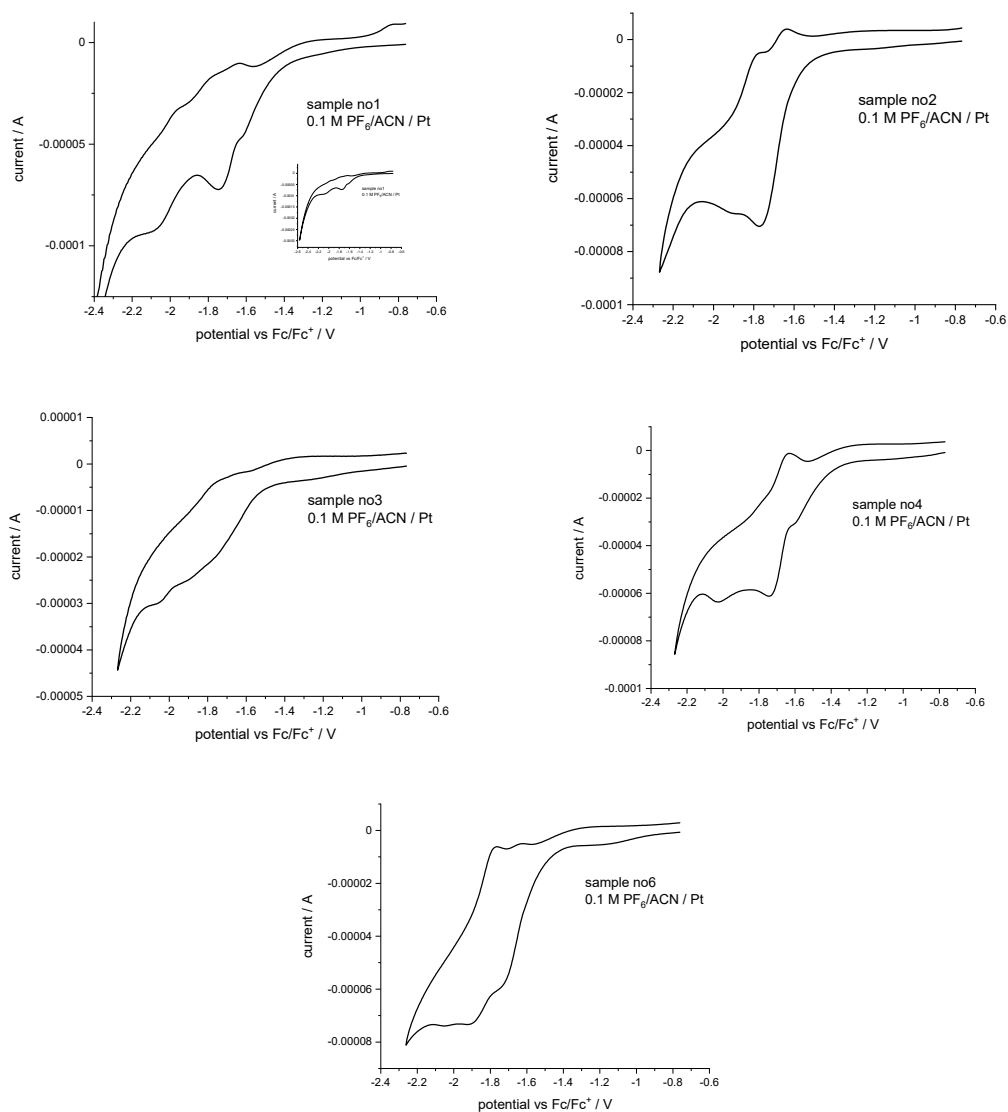
H	6.424448000	-2.129599000	-0.892273000
H	2.611335000	0.769435000	0.475659000
H	4.926812000	1.644650000	0.585103000
H	-1.174817000	0.505400000	0.728907000
H	-0.102410000	-3.397804000	-0.869950000
H	-5.998732000	-3.979728000	-0.645976000
H	-1.884841000	-5.037108000	-1.373371000
H	-4.289340000	-5.631227000	-1.423773000
H	-6.989109000	0.090460000	1.639995000
H	-5.719925000	1.283565000	2.003363000
H	10.525985000	-0.577256000	-0.681960000
H	9.032815000	3.195304000	0.756805000
H	12.842619000	0.300673000	-0.575244000
H	11.350490000	4.070624000	0.862139000
H	13.259153000	2.625551000	0.196552000
H	-5.814278000	2.092112000	-0.355300000
H	-7.074214000	0.908590000	-0.715809000
H	-8.577146000	1.999720000	0.976103000
H	-7.323302000	3.178426000	1.333616000
H	-7.405363000	3.986112000	-1.043351000
H	-8.657716000	2.807778000	-1.401146000
H	-10.159447000	3.889609000	0.295784000
H	-8.908070000	5.067548000	0.652708000
H	-9.010371000	5.906821000	-1.727763000
H	-10.270494000	4.720585000	-2.087297000
H	-10.589539000	6.028373000	-0.938948000

## 8. Electrochemical investigations in dry acetonitrile

**Table S7.** The electrochemical data investigated in acetonitrile.

Molecule	Method	$E_{red}^1$ (V)	$E_{red}^{1(onset)}$ (V)	$E_{ox}^1$ (V)	$E_{ox}^{1(onset)}$ (V)	$E_{LUMO}$ (eV)	$E_{HOMO}$ (eV)	$E_g$ (eV)
AzNI-1	CV	-1.61	-1.45	0.82	0.66	-3.65	-5.76	2.12
	DPV	-1.53	-1.19	0.73	0.62	-3.91	-5.72	1.81
AzNI-2	CV	-1.77	-1.60	0.87	0.66	-3.50	-5.76	2.26
	DPV	-1.58	-1.57	0.78	0.56	-3.52	-5.66	2.14
AzNI-3	CV	-1.88	-1.55	0.95	0.81	-3.55	-5.91	2.36
	DPV	-1.63	-1.45	0.72	0.62	-3.66	-5.72	2.07
AzNI-4	CV	-1.59	-1.42	0.69	0.45	-3.68	-5.55	1.87
	DPV	-1.58	-1.33	0.49	0.31	-3.77	-5.41	1.62
AzNI-6	CV	-1.73	-1.56	0.74	0.64	-3.54	-5.74	2.20
	DPV	-1.73	-1.57	0.64	0.49	-3.52	-5.59	2.07

$E_{HOMO} = (-5.1 - E_{ox}^{1(onset)}) \cdot e^-$ ,  $E_{LUMO} = (-5.1 - E_{red}^{1(onset)}) \cdot e^-$ ,  $E_g = E_{ox}^{1(onset)} - E_{red}^{1(onset)}$ . Solvent: dry ACN and 0.1 mol/dm<sup>3</sup> Bu<sub>4</sub>NPF<sub>6</sub> and platinum wire as a working electrode.  $E_{ox}^1$  – the first oxidation process,  $E_{red}^1$  – the first reduction process,  $E_{red}^{1(onset)}$  – the onset potential of the first reduction process,  $E_{ox}^{1(onset)}$  – the onset potential of the first oxidation process.  $E_{HOMO}$  and  $E_{LUMO}$  as IP and EA.  $v = 0.1$  V/s for CV and  $v = 0.05$  V/s for DPV.



**Figure S13.** CV of the samples 1-6 (AzNI-1 – AzNI-6) (except AzNI-5, sample no5) in 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) in dry acetonitrile (ACN) after Ar bubbling, at room temperature.

## References

51. Gaussian 09, Revision A.02, Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Scalmani G., Barone V., Petersson G. A., Nakatsuji H., Li X., Caricato M., Marenich A., Bloino J., Janesko B. G., Gomperts R., Mennucci B., Hratchian H. P., Ortiz J. V., Izmaylov A. F., Sonnenberg J. L., Williams-Young D., Ding F., Lipparini F., Egidi F., Goings J., Peng B., Petrone A., Henderson T., Ranasinghe D., Zakrzewski V. G., Gao J., Rega N., Zheng G., Liang W., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Throssell K., Montgomery J. A. Jr., Peralta J. E., Ogliaro F., Bearpark M., Heyd J. J., Brothers E., Kudin K. N., Staroverov V. N., Keith T., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J. C., Iyengar S. S., Tomasi J., Cossi M., Millam J. M., Klene M., Adamo C., Cammi R., Ochterski J. W., Martin R. L., Morokuma K., Farkas O., Foresman J. B., and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016
52. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, **1993**, *98*, 5648-5652. <https://doi.org/10.1063/1.464913>.
53. Lee, C.; Yang, W.; Parr, R.G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*, **1988**, *37*, 785-789. <https://doi.org/10.1103/PhysRevB.37.785>.
54. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.*, **2011**, *32*, 1456-1465. <https://doi.org/10.1002/jcc.21759>.
55. Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model, *J. Phys. Chem. A*, **1998**, *102*, 1995. <https://doi.org/10.1021/jp9716997>.
56. O'Boyle, N.M.; Tenderholt, A.L.; Langner, K.M. A Library for Package-Independent Computational Chemistry Algorithms. *J. Comput. Chem.*, **2008**, *29*, 839-845. <https://doi.org/10.1002/jcc.20823>.
57. Casida, M.E. In Recent Developments and Applications of Modern Density Functional Theory, Theoretical and Computational Chemistry, Jorge M. Seminario Eds.; Elsevier: Amsterdam, 1996; Volume 4, pp. 391.