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§1. Single crystal X-ray crystallography

Table S1. X-Ray crystallographic data for **1**·CH₂Cl₂, **2**, **3**·3H₂O and **4**·CH₃CN.

	1 ·CH ₂ Cl ₂	2	3 ·3H ₂ O	4 ·CH ₃ CN
Crystal data	2090740	2090741	2126017	2126016
Chemical formula	C ₁₅ H ₁₂ AsCuIN ₃	C ₃₀ H ₂₄ As ₂ Cu ₂ Br ₂ N ₆	C ₆₀ H ₄₈ Ag ₅ As ₄ N ₁₂ ·5(ClO ₄)	C ₃₆ H ₃₂ Ag ₂ As ₂ N ₆ ·2(ClO ₄)·2(C ₂ H ₃ N)
<i>M_r</i>	584.56	905.29	2273.38	1195.26
Crystal system, space group	Orthorhombic, <i>Pbcm</i>	Monoclinic, <i>P2₁/n</i>	Triclinic, <i>P1</i>	Monoclinic, <i>P2₁/c</i>
Temperature (K)	200	296	200	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.0576(10), 16.629(2), 14.450(2)	8.8551(8), 11.7729(13), 15.7798(15)	15.5058(13), 22.0968(19), 35.863(3)	14.5721(7), 8.5513(3), 19.9140(8)
β(°)	-	104.157(5)	-	110.961(2)
<i>V</i> (Å ³)	1936.1(4)	1595.1(3)	11720.5(17)	2317.28(17)
<i>Z</i>	4	2	6	2
μ (mm ⁻¹)	4.70	5.93	3.16	2.44

Crystal size (mm)	$0.25 \times 0.20 \times 0.01$	$0.15 \times 0.08 \times 0.04$	$0.15 \times 0.15 \times 0.08$	$0.50 \times 0.04 \times 0.02$
$T_{\min}, T_{\max}$	0.653, 0.928	0.776, 0.958	0.810, 0.928	0.715, 0.862
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11744, 2320, 1997	15644, 3669, 2627	158498, 41400, 18320	18686, 5315, 4223
R_{int}	0.054	0.053	0.109	0.050
$(\sin \theta/\lambda)_{\max} (\text{\AA}^{-1})$	0.650	0.650	0.595	0.652
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.070, 1.01	0.032, 0.068, 1.00	0.068, 0.179, 0.90	0.030, 0.069, 1.01
No. of reflections	2320	3669	41400	5315
No. of parameters	123	190	2863	280
$\Delta\rho_{\max}, \Delta\rho_{\min} (\text{e \AA}^{-3})$	0.74, -0.53	0.49, -0.42	3.28, -1.72	0.45, -0.43

§2. Powder X-ray diffraction patterns of $1 \cdot \text{CH}_2\text{Cl}_2$ and **2**

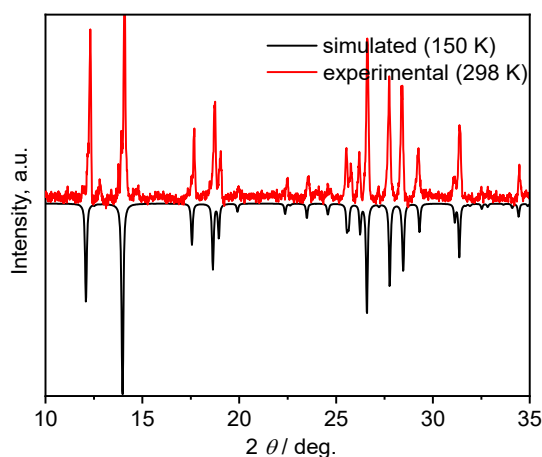


Figure S1. Experimental and simulated PXRD patterns of an as-synthesized sample of $1 \cdot \text{CH}_2\text{Cl}_2$.

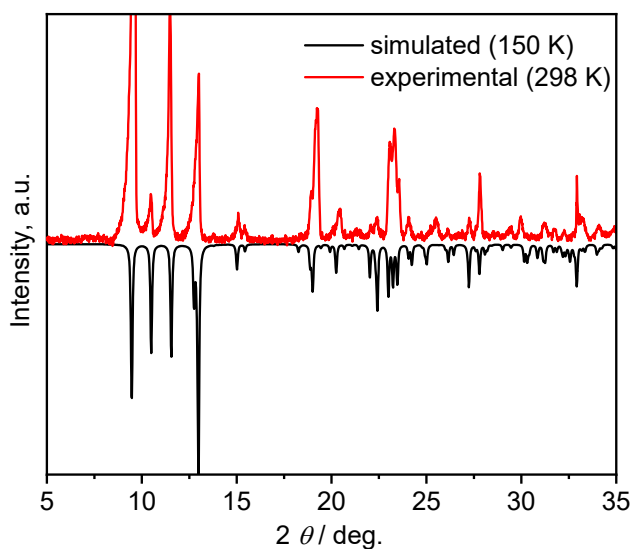


Figure S2. Experimental and simulated PXRD patterns of an as-synthesized sample of **2**.

§3. ^1H NMR spectra

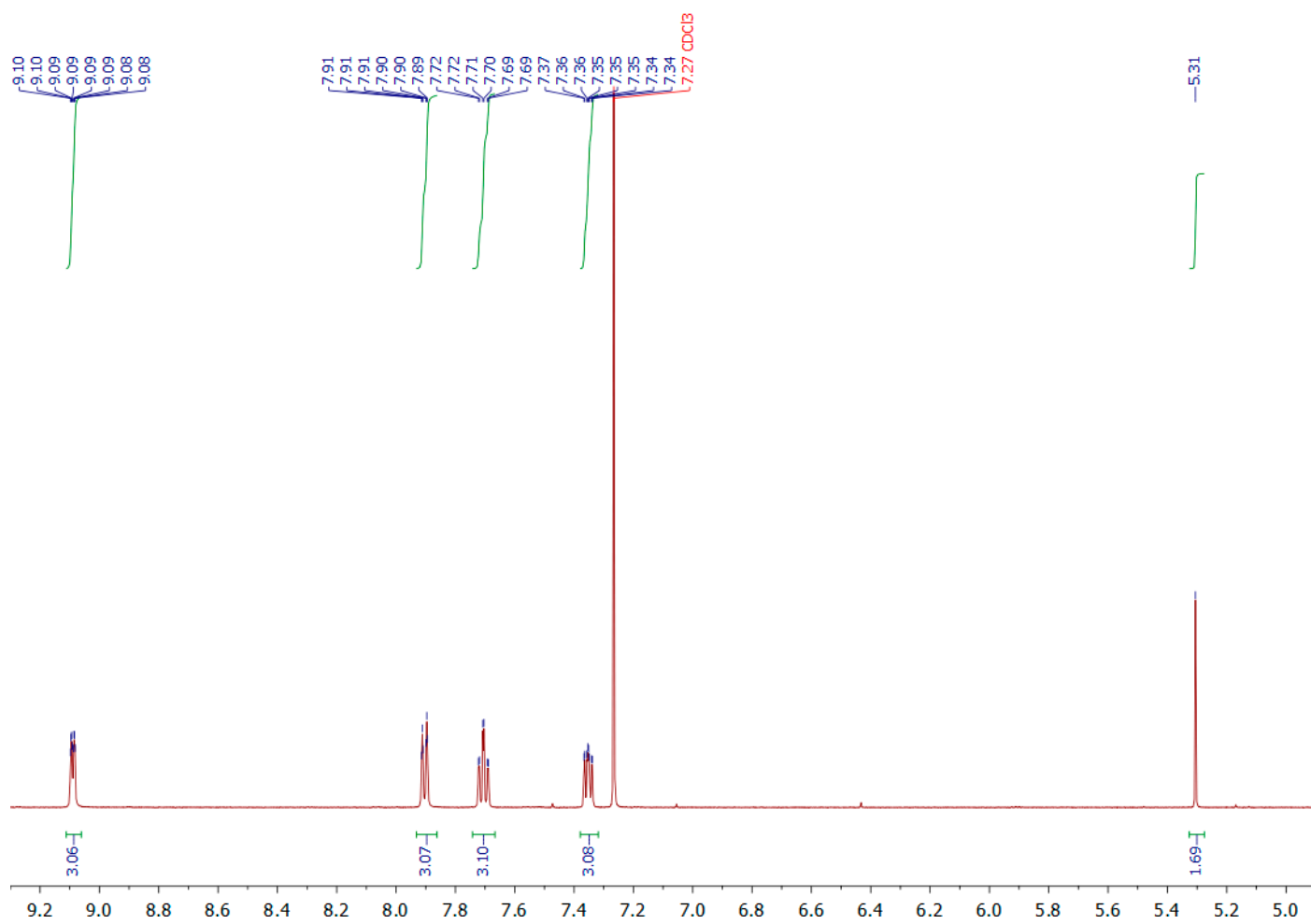


Figure S3. ^1H NMR spectrum of **1**· CH_2Cl_2 (CDCl_3 , 25 °C).

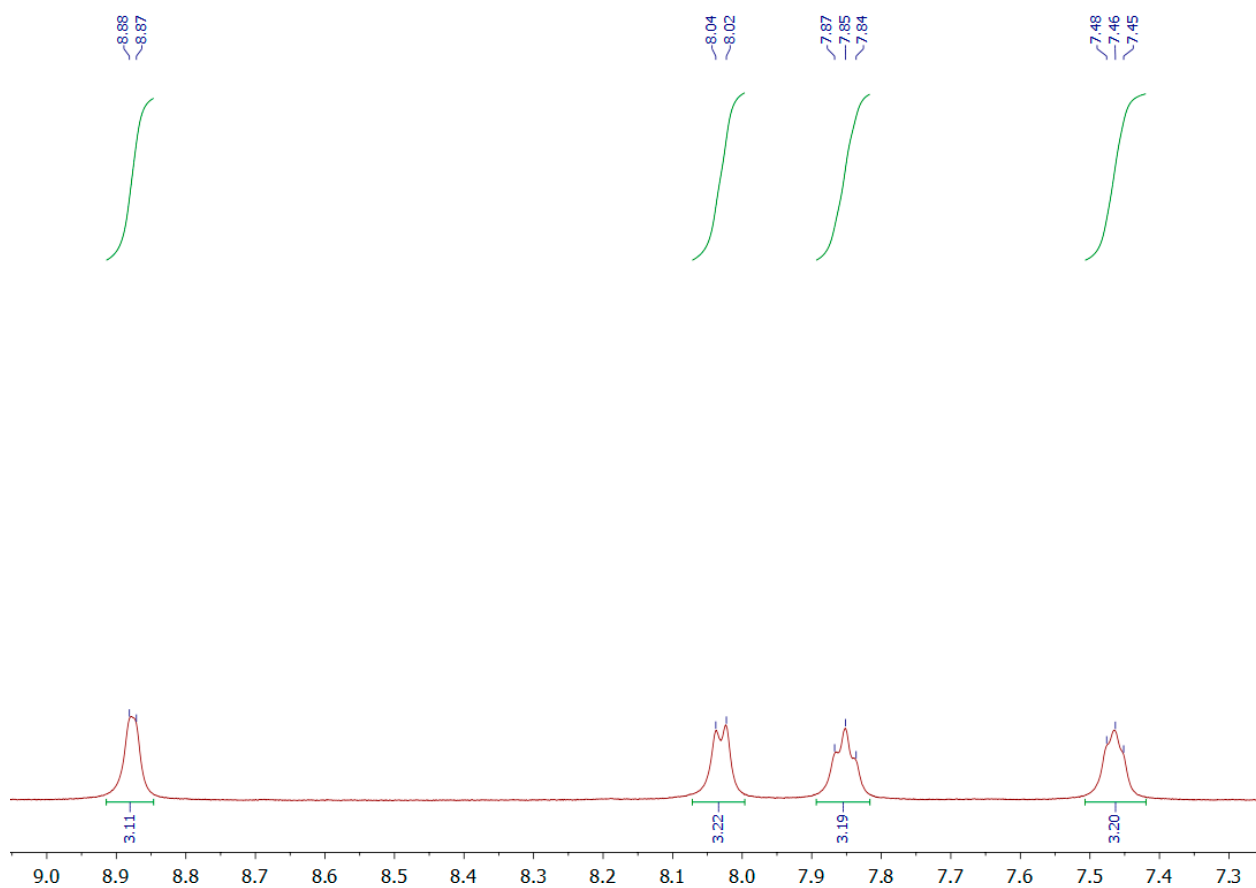


Figure S4. ¹H NMR spectrum of **1a** (CD₃CN, 25 °C).

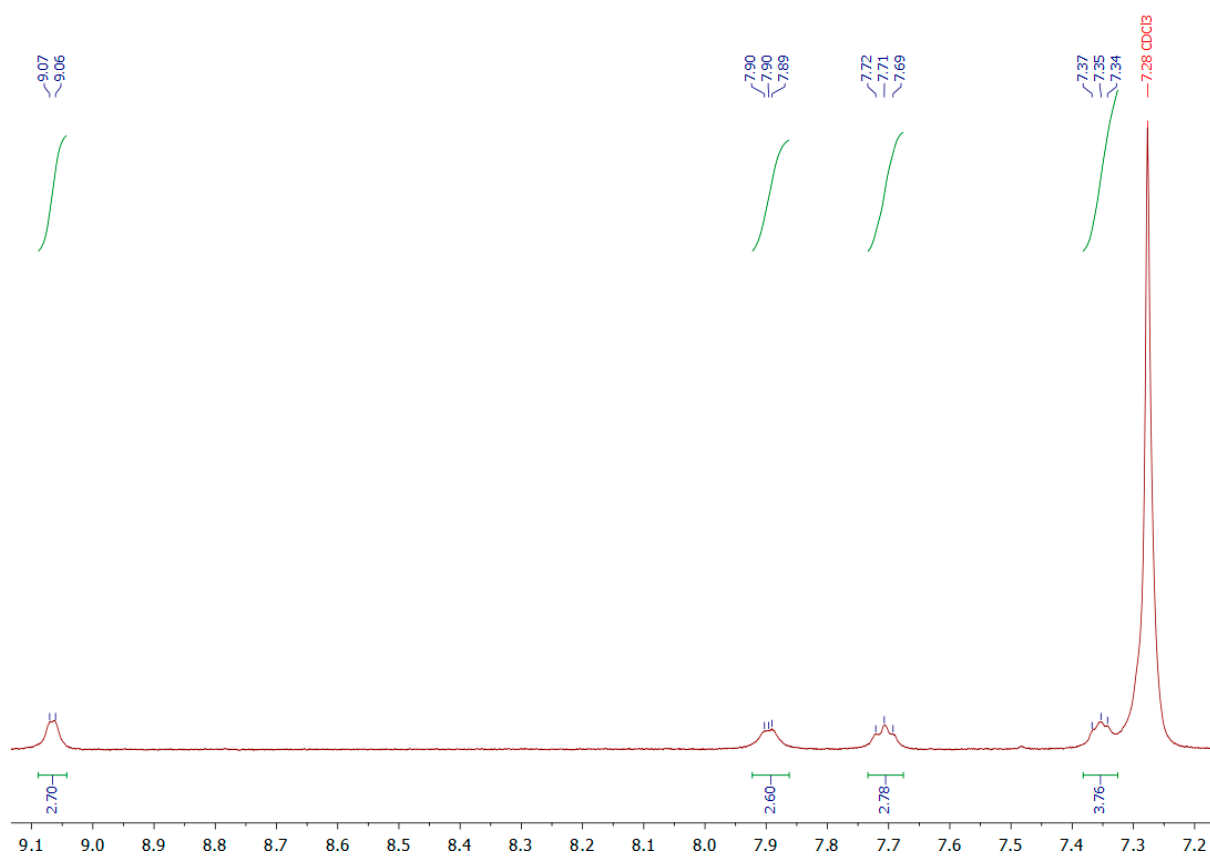


Figure S5. ¹H NMR spectrum of **2** (CDCl₃, 25 °C).

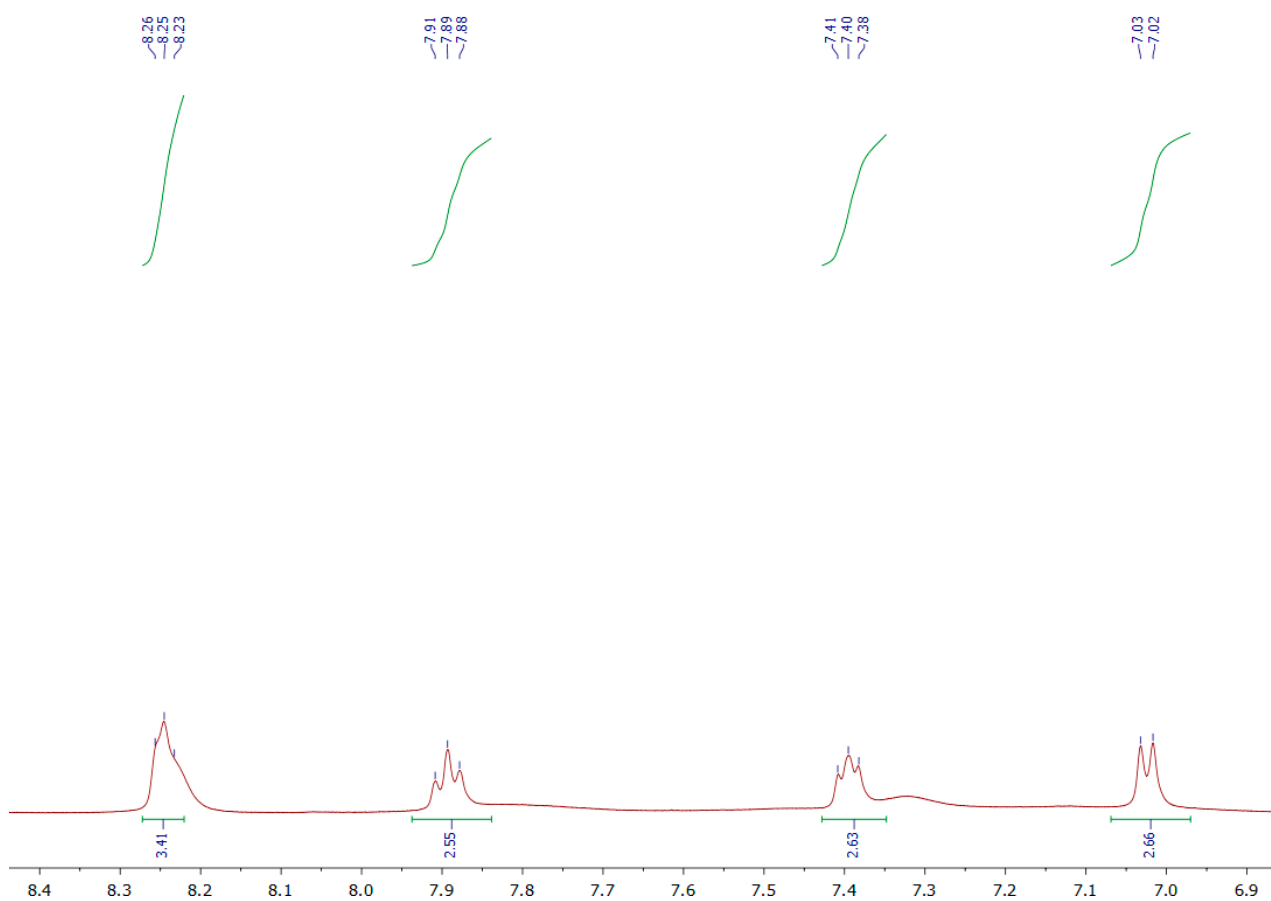


Figure S6. ¹H NMR spectrum of **3**·3H₂O (CD₃CN, 25 °C).

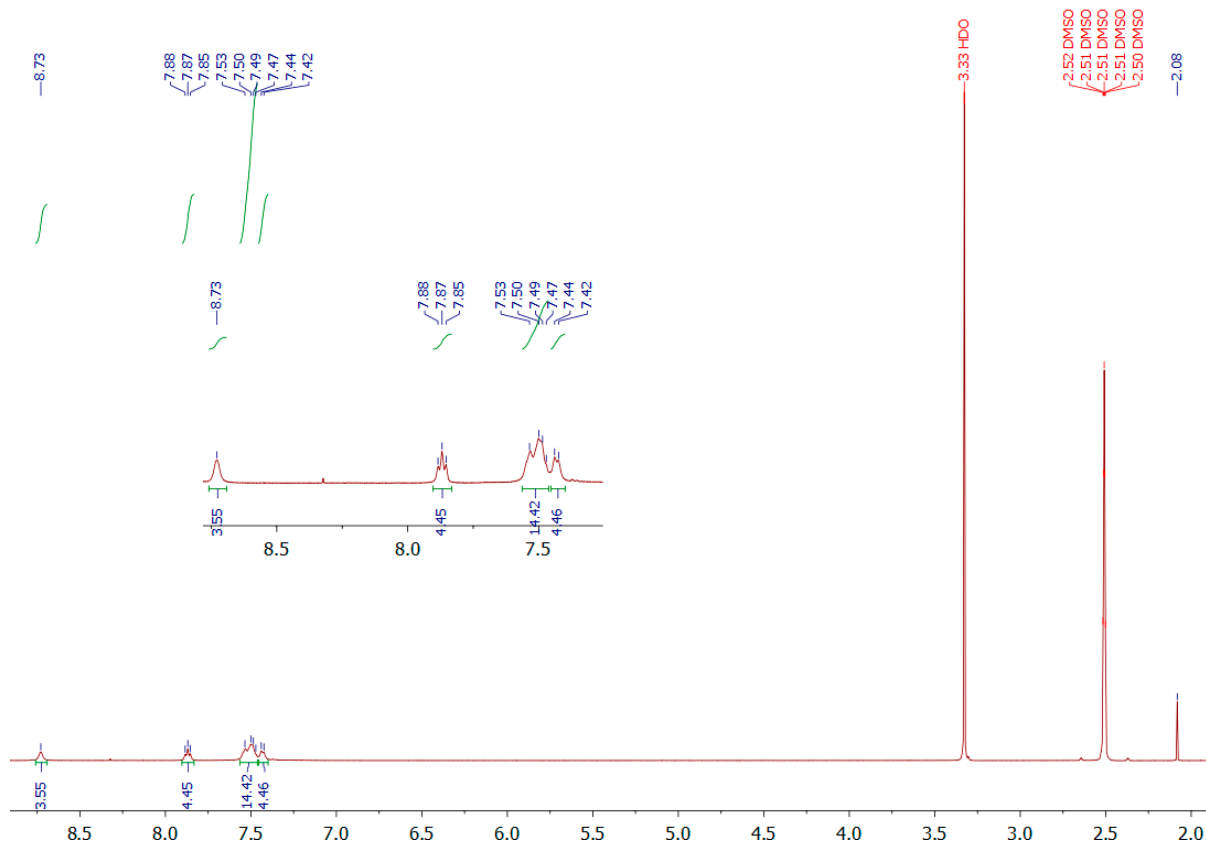


Figure S7. ¹H NMR spectrum of **4**·CH₃CN (DMSO-d₆, 25 °C).

§4. FT-IR spectra

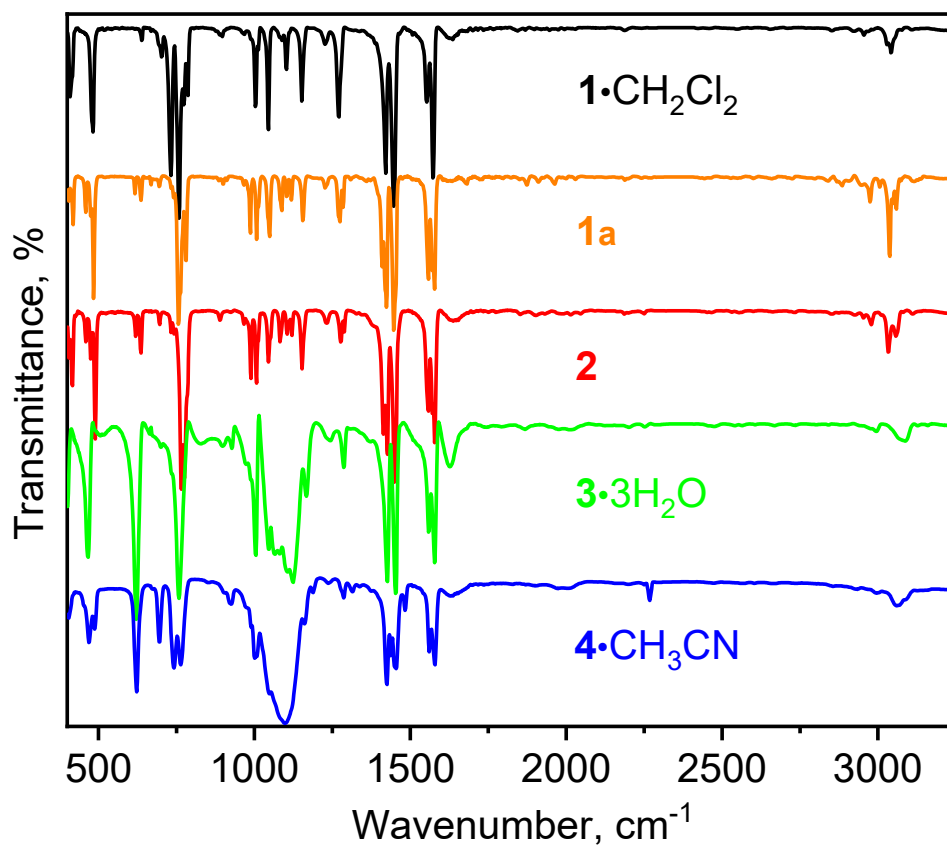


Figure S8. FT-IR spectra for the complexes **1**·CH₂Cl₂, **1a**, **2**, **3**·3H₂O and **4**·CH₃CN in the 400–3250 cm⁻¹ region.

§5. TGA&DTG curves

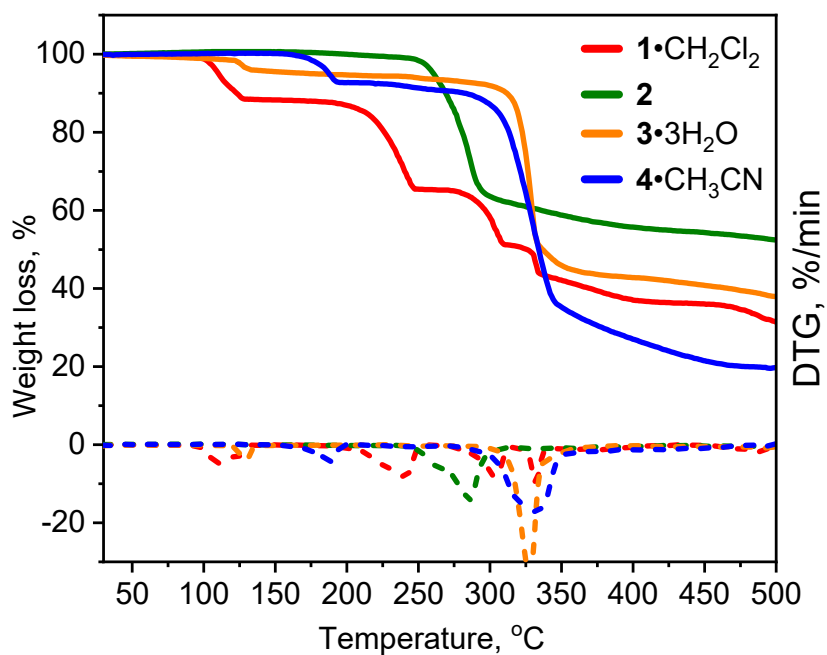


Figure S9. TGA&DTG curves for **1**·CH₂Cl₂, **2**, **3**·3H₂O and **4**·CH₃CN.

§6. Computational details

DFT and TD-DFT computations were performed using Gaussian 09 program.¹ The structures of the S_0 were fully optimized using PBE0² hybrid functionals coupled with the def2-TZVP basis set.³ There are no imaginary frequencies were found in all optimized structures. The absorption spectrum was computed using time-dependent DFT (TD-DFT)⁴ calculations with the optimized ground state (S_0) geometry.

§6.1. Relative stabilities of complexes $[\text{Cu}(\text{Py}_3\text{As})\text{X}]$ and $[\text{Cu}_2(\text{Py}_3\text{As})_2\text{X}_2]$ ($\text{X} = \text{Br}, \text{I}$)

To estimate the relative stabilities of scorpionate $[\text{Cu}(\text{Py}_3\text{As})\text{X}]$ and dimeric $[\text{Cu}_2(\text{Py}_3\text{As})_2\text{X}_2]$ complexes ($\text{X} = \text{Br}, \text{I}$), their geometries were optimized at PBE0/def2TZVP level of the theory. The Gibbs free energies of these complexes were calculated at the same level. The results of calculations are outlined in Figure S1.

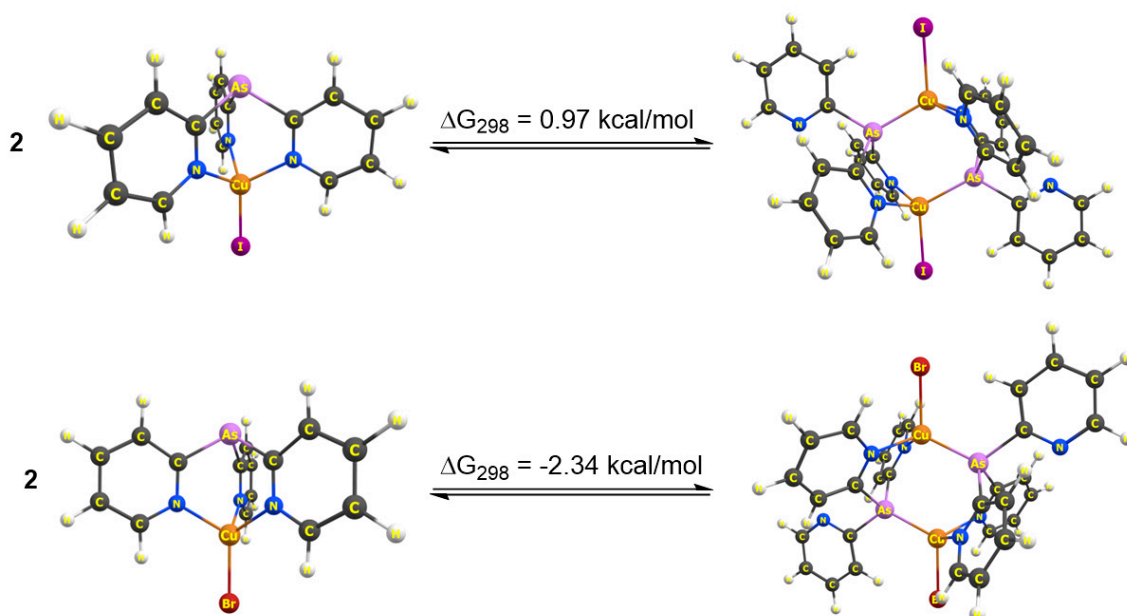


Figure S10. Gibbs free energies calculated for the equilibria $2 [\text{Cu}(\text{Py}_3\text{As})\text{X}] \leftrightarrow [\text{Cu}_2(\text{Py}_3\text{As})_2\text{X}_2]$ ($\text{X} = \text{Br}, \text{I}$) at PBE0/def2TZVP level.

§6.2. Molecular orbital' calculations

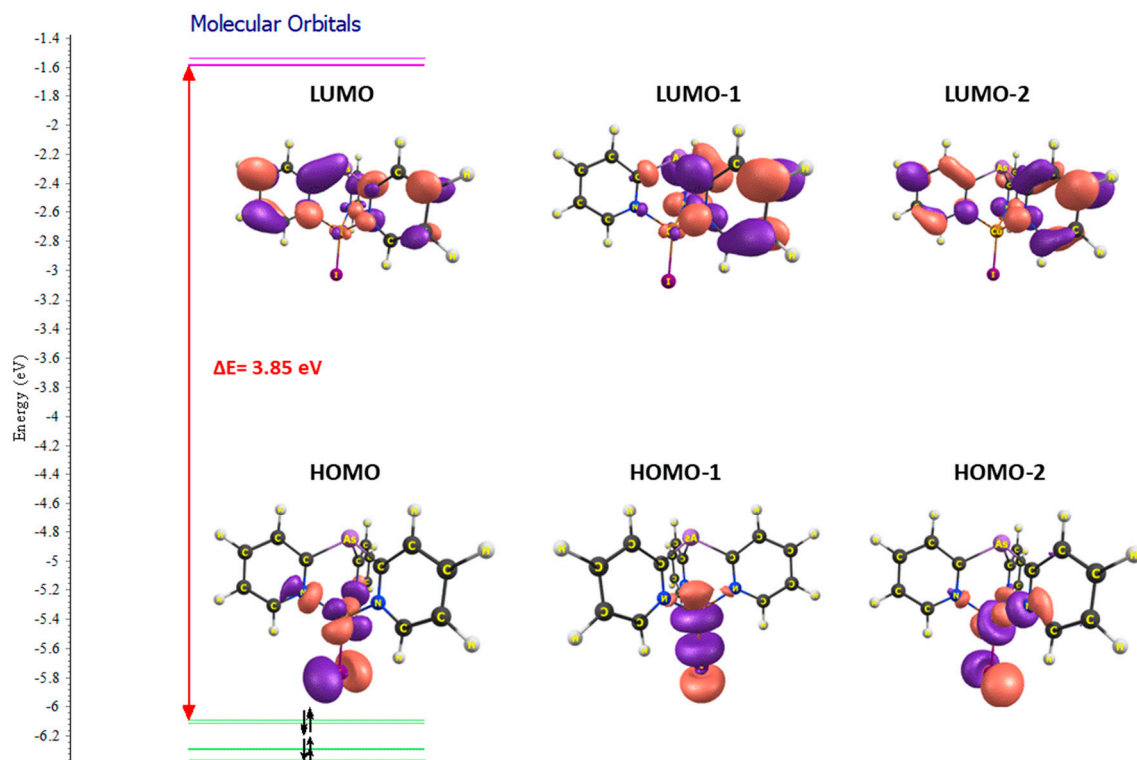


Figure S11. Selected frontier molecular orbitals (isovalue = 0.04) calculated for the optimized S_0 state geometry of $[\text{Cu}(\text{AsPy}_3)\text{I}]$ (**1**) at PBE0/def2TZVP level.

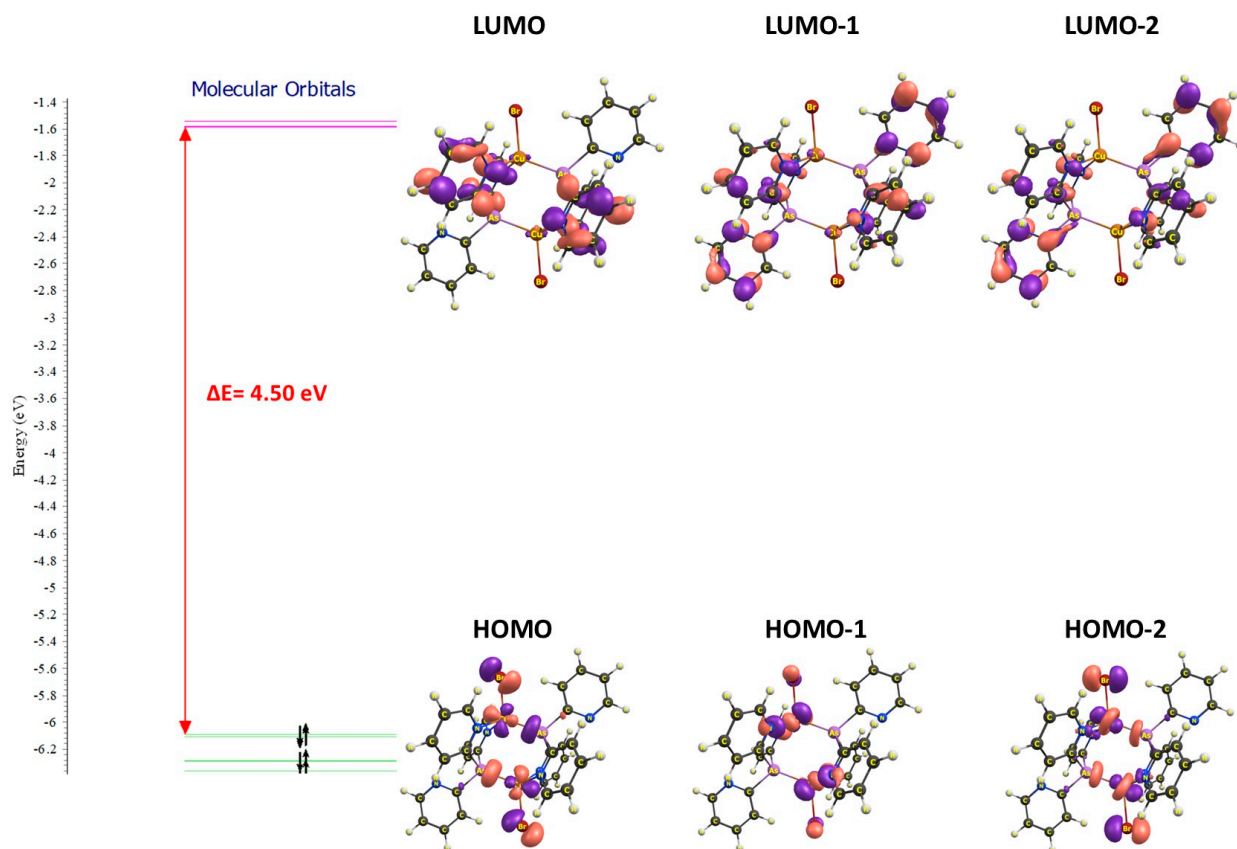


Figure S12. Selected frontier molecular orbitals (isovalue = 0.04) calculated for the optimized S_0 state geometry of $[\text{Cu}_2(\text{Py}_3\text{As})_2\text{Br}_2]$ (**2**) at PBE0/def2TZVP level.

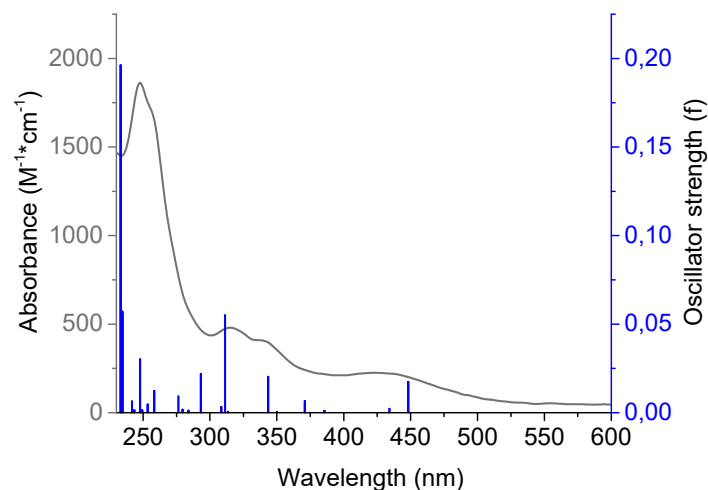


Figure S13. The UV-Vis spectrum of [Cu(AsPy₃)I] (**1**) (CH₂Cl₂, 298 K) and absorption patterns (vertical bars) calculated at the TD-PBE0/def2TZVP level.

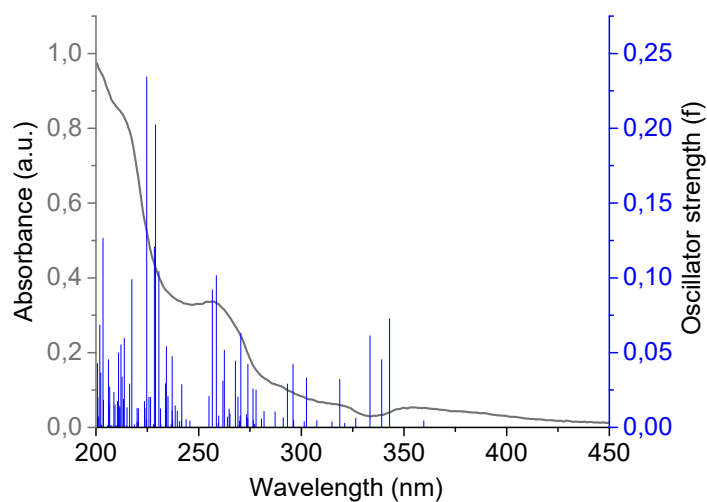


Figure S14. The UV-Vis spectrum of [Cu₂(Py₃As)₂Br₂] (**2**) (MeCN, 298 K) and absorption patterns (vertical bars) calculated at the TD-PBE0/def2TZVP level.

Table S2. Atomic contributions to selected molecular orbitals of [Cu(AsPy₃)I] (**1**) in the ground state (S₀) geometry according Mulliken population analysis at PBE0/def2TZVP level.

MO	Energy, eV	Contribution, %		
		Cu	I	Py ₃ As
LUMO+2	-1,13853	0	0	100
LUMO+1	-1,64168	2	0	98
LUMO	-1,64195	2	0	98
HOMO	-5,48858	58	24	18
HOMO-1	-5,48885	58	24	18
HOMO-2	-5,93104	63	31	6
HOMO-3	-6,33459	63	29	9
HOMO-4	-6,33486	63	29	9
HOMO-5	-6,96671	47	47	6
HOMO-6	-6,96726	47	47	6

HOMO-7	-7,59639	3.3	0.04	96.3
HOMO-8	-7,8198	43	55	2
HOMO-9	-7,91667	0	0	100
HOMO-10	-8,01844	4	0	95
HOMO-11	-8,01844	4	0	95

Table S3. Atomic contributions to selected molecular orbitals of [Cu₂(Py₃As)₂Br₂] (**2**) in the ground state (S₀) geometry according Mulliken population analysis at PBE0/def2TZVP level.

MO	Energy, eV	Contribution, %	
		CuBr	L
LUMO+2	-1,54127	2	98
LUMO+1	-1,58508	1	99
LUMO	-1,58834	3	97
HOMO	-6,08941	69	31
HOMO-1	-6,10683	70	30
HOMO-2	-6,28289	74	26
HOMO-3	-6,29078	77	23
HOMO-4	-6,36126	89	11
HOMO-5	-6,46901	85	15
HOMO-6	-6,91338	93	7
HOMO-7	-6,97814	90	10
HOMO-8	-6,98903	87	13
HOMO-9	-7,02359	85	15
HOMO-10	-7,54088	48	52
HOMO-11	-7,54578	48	52

Table S4. Calculated (TD-PBE0/def2-TZVP) energies and characters of the main singlet excitations ($f > 0.01$) of [Cu(AsPy₃)I] (**1**).

E, eV	λ , nm	$f^{(a)}$	Transitions (main contributions)	Character ^(b)
2.766	448.18	0.018	H-1 -> L+1 (48%) HOMO -> LUMO (48%)	(CuI)LCT
2.767	448.16	0.018	HOMO -> L+1 (48%) H-1 -> LUMO (48%)	(CuI)LCT
3.609	343.53	0.021	H-4 -> LUMO (26%) H-3 -> L+1 (25%) H-4 -> L+1 (20%) H-3 -> LUMO (20%)	(CuI)LCT
3.609	343.53	0.020	H-4 -> L+1 (26%) H-3 -> LUMO (25%) H-3 -> L+1 (21%) H-4 -> LUMO (20%)	(CuI)LCT
3.982	311.33	0.055	H-4 -> L+1 (26%) H-3 -> LUMO (26%) H-3 -> L+1 (21%) H-4 -> LUMO (21%)	(CuI)LCT
4.229	293.16	0.022	H-3 -> L+2 (95%)	(CuI)LCT

			H-6 -> L+2 (4%)	
4.299	293.15	0.022	H-4 -> L+2 (95%)	(CuI)LCT
5.314	233.32	0.196	H-9 -> LUMO (24%) H-8 -> L+1 (14%) H-11 -> LUMO (13%) H-9 -> L+1 (13%) H-10 -> L+1 (13%)	(L)LCT+(CuI)LCT
5.314	233.31	0.196	H-9 -> L+1 (24%) H-8 -> LUMO (14%) H-11 -> L+1 (13%) H-10 -> LUMO (13%) H-9 -> LUMO (13%)	(L)LCT+(CuI)LCT

^(a) Oscillator strength; ^(b) L is Py₃As.

Table S5. Calculated (TD-PBE0/def2-TZVP) energies and characters of the main singlet excitations ($f > 0.01$) of [Cu₂(Py₃As)₂Br₂] (**2**).

E, eV	λ , nm	$f^{(a)}$	Transitions (main contributions)	Character ^(b)
3.615	342.94	0.073	HOMO -> LUMO (50%) H-1 -> L+2 (30%)	(CuBr)LCT
3.718	333.472	0.061	HOMO -> L+2 (88%)	(CuBr)LCT
4.525	273.99	0.042	H-2 -> L+7 (61%) H-4 -> L+6 (20%)	(CuBr)LCT
4.582	270.59	0.063	H-6 -> L+2 (31%) H-7 -> L+1 (19%) H-3 -> L+8 (17%)	(CuBr)LCT
4.607	269.13	0.021	H-7 -> L+1 (67%) H-6 -> L+2 (18%)	(CuBr)LCT
4.794	258.62	0.102	HOMO -> L+12 (52%) H-8 -> L+3 (23%) H-9 -> LUMO (14%)	(CuBr)LCT
4.831	256.66	0.092	H-8 -> L+3 (44%) HOMO -> L+12 (26%)	(CuBr)LCT
5.414	228.99	0.0202	H-15 -> LUMO (39%) H-16 -> L+3 (13%) H-8 -> L+8 (12%)	(CuBr)LCT
5.427	228.48	0.121	H-13 -> L+2 (17%) H-19 -> L+1 (15%) H-16 -> L+1 (11%) H-12 -> L+1 (10%) H-18 -> L+2 (10%)	(CuBr)LCT
5.517	224.72	0.234	H-16 -> L+1 (25%) H-15 -> L+2 (16%) H-19 -> L+1 (14%) H-18 -> L+2 (13%)	L(L)CT
5.538	223.87	0.013	H-6 -> L+12 (42%) H-12 -> L+3 (17%) H-3 -> L+13 (9%)	(CuBr)LCT+(L)LCT

5.545	223.62	0.017	H-14 → LUMO (49%) H-11 → L+3 (19%)	(CuBr)LCT+(L)LCT
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^(a) Oscillator strength; ^(b) L is Py₃As.

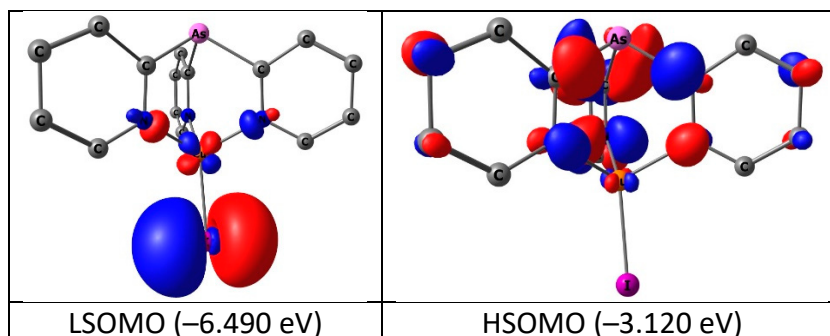


Figure S15. LSOMO and HSOMO (isovalue = 0.04) calculated for the optimized gas phase T₁ state geometry of [Cu(AsPy₃)I] (**1**) at PBE0/def2TZVP level.

Cartesian coordinates for gas phase S₀ and T₁ state geometries of [Cu(AsPy₃)I] (**1**) at PBE0/def2TZVP level.

S ₀ state				T ₁ state			
I	3.346487000	0.000374000	0.000316000	I	3.346487000	0.000374000	0.000316000
As	-2.518224000	-0.000561000	-0.000578000	As	-2.518224000	-0.000561000	-0.000578000
Cu	0.835421000	0.000435000	0.000233000	Cu	0.835421000	0.000435000	0.000233000
N	-0.242601000	-1.613122000	-0.759448000	N	-0.242601000	-1.613122000	-0.759448000
N	-0.243744000	0.148766000	1.776790000	N	-0.243744000	0.148766000	1.776790000
C	0.366450000	-2.685437000	-1.264223000	C	0.366450000	-2.685437000	-1.264223000
H	1.452037000	-2.655197000	-1.249929000	H	1.452037000	-2.655197000	-1.249929000
C	-0.334699000	-3.765931000	-1.773100000	C	-0.334699000	-3.765931000	-1.773100000
H	0.201663000	-4.617116000	-2.173822000	H	0.201663000	-4.617116000	-2.173822000
C	-1.719163000	-3.728332000	-1.755621000	C	-1.719163000	-3.728332000	-1.755621000
H	-2.300891000	-4.556019000	-2.145452000	H	-2.300891000	-4.556019000	-2.145452000
C	-2.351096000	-2.612041000	-1.230269000	C	-2.351096000	-2.612041000	-1.230269000
H	-3.432334000	-2.543982000	-1.198416000	H	-3.432334000	-2.543982000	-1.198416000
C	-1.573863000	-1.570012000	-0.739511000	C	-1.573863000	-1.570012000	-0.739511000
C	-1.574985000	0.144351000	1.728681000	C	-1.574985000	0.144351000	1.728681000
C	-2.352916000	0.240171000	2.876037000	C	-2.352916000	0.240171000	2.876037000
H	-3.434109000	0.233580000	2.800543000	H	-3.434109000	0.233580000	2.800543000
C	-1.721718000	0.343297000	4.105843000	C	-1.721718000	0.343297000	4.105843000
H	-2.303993000	0.419458000	5.017212000	H	-2.303993000	0.419458000	5.017212000
C	-0.337284000	0.347193000	4.147969000	C	-0.337284000	0.347193000	4.147969000
H	0.198507000	0.425885000	5.085797000	H	0.198507000	0.425885000	5.085797000
C	0.364568000	0.247810000	2.958220000	C	0.364568000	0.247810000	2.958220000
H	1.450176000	0.245429000	2.925551000	H	1.450176000	0.245429000	2.925551000
N	-0.243343000	1.464556000	-1.017051000	N	-0.243343000	1.464556000	-1.017051000
C	0.365100000	2.438431000	-1.693089000	C	0.365100000	2.438431000	-1.693089000
H	1.450703000	2.411589000	-1.674161000	H	1.450703000	2.411589000	-1.674161000
C	-0.336648000	3.418995000	-2.374312000	C	-0.336648000	3.418995000	-2.374312000
H	0.199250000	4.192043000	-2.910959000	H	0.199250000	4.192043000	-2.910959000
C	-1.721095000	3.384111000	-2.350641000	C	-1.721095000	3.384111000	-2.350641000
H	-2.303279000	4.135224000	-2.872490000	H	-2.303279000	4.135224000	-2.872490000
C	-2.352392000	2.370326000	-1.646994000	C	-2.352392000	2.370326000	-1.646994000
H	-3.433591000	2.307950000	-1.604127000	H	-3.433591000	2.307950000	-1.604127000
C	-1.574590000	1.424709000	-0.990025000	C	-1.574590000	1.424709000	-0.990025000

Cartesian coordinates for gas phase S₀ state geometries of [Cu₂(Py₃As)₂Br₂] (**2**) at PBE0/def2TZVP level.

S ₀ state			
Br	-2.474720000	-3.618512000	-0.000006000
As	-2.042576000	0.394624000	0.000001000

Cu	-0.979511000	-1.709962000	-0.000001000
N	-0.398111000	2.052366000	1.548248000
N	-0.398114000	2.052369000	-1.548249000
C	-1.649512000	1.593160000	1.504159000
C	-2.576416000	1.880260000	2.496623000
H	-3.585650000	1.498120000	2.431519000
C	-2.185152000	2.676513000	3.559721000
H	-2.887616000	2.912797000	4.351196000
C	-0.893387000	3.175947000	3.588305000
H	-0.551186000	3.814325000	4.393145000
C	-0.033299000	2.845423000	2.557132000
H	0.982160000	3.225856000	2.505563000
C	-0.033305000	2.845430000	-2.557130000
H	0.982157000	3.225860000	-2.505564000
C	-0.893398000	3.175965000	-3.588295000
H	-0.551198000	3.814342000	-4.393136000
C	-2.185166000	2.676539000	-3.559703000
H	-2.887635000	2.912832000	-4.351171000
C	-2.576428000	1.880283000	-2.496606000
H	-3.585664000	1.498152000	-2.431495000
C	-1.649517000	1.593170000	-1.504151000
C	-4.004899000	0.450074000	0.000001000
C	-4.706261000	-0.748139000	-0.000006000
H	-4.175214000	-1.698002000	-0.000007000
C	-6.093754000	-0.689774000	-0.000009000
H	-6.675675000	-1.604678000	-0.000014000
C	-6.713089000	0.547287000	-0.000002000
H	-7.792907000	0.638365000	-0.000004000
C	-5.917002000	1.685964000	0.000007000
H	-6.366803000	2.675273000	0.000013000
N	-4.590494000	1.646461000	0.000008000
Br	2.474719000	3.618512000	0.000004000
As	2.042576000	-0.394623000	0.000000000
Cu	0.979511000	1.709962000	0.000000000
N	0.398113000	-2.052367000	-1.548248000
N	0.398113000	-2.052367000	1.548249000
C	1.649514000	-1.593162000	-1.504157000
C	2.576420000	-1.880265000	-2.496618000
H	3.585654000	-1.498125000	-2.431512000
C	2.185158000	-2.676519000	-3.559715000
H	2.887624000	-2.912806000	-4.351188000
C	0.893393000	-3.175953000	-3.588302000
H	0.551193000	-3.814332000	-4.393141000
C	0.033303000	-2.845426000	-2.557132000
H	-0.982158000	-3.225858000	-2.505564000
C	0.033303000	-2.845427000	2.557131000
H	-0.982158000	-3.225858000	2.505564000
C	0.893394000	-3.175959000	3.588299000
H	0.551194000	-3.814335000	4.393140000
C	2.185162000	-2.676531000	3.559708000
H	2.887629000	-2.912822000	4.351179000
C	2.576425000	-1.880276000	2.496611000
H	3.585660000	-1.498145000	2.431501000
C	1.649516000	-1.593167000	1.504154000
C	4.004899000	-0.450074000	-0.000002000
C	4.706262000	0.748138000	-0.000011000
H	4.175216000	1.698002000	-0.000017000
C	6.093755000	0.689772000	-0.000014000
H	6.675677000	1.604676000	-0.000021000
C	6.713089000	-0.547290000	-0.000006000
H	7.792906000	-0.638369000	-0.000007000
C	5.917001000	-1.685966000	0.000002000
H	6.366801000	-2.675276000	0.000007000
N	4.590493000	-1.646462000	0.000004000

§6.3. QTAIM and ELF calculations

The QTAIM and ELF calculations of cations of **3** and **4**, $[\text{Ag}@\text{Ag}_4(\text{Py}_3\text{As})_4]^{5+}$ and $[\text{Ag}_2(\text{PhPy}_2\text{As})_2(\text{MeCN})_2]^{2+}$, using available X-ray coordinates. The single point computations have been carried out using the dispersion-corrected hybrid functional ωB97XD^5 incorporated in Gaussian-09 package.¹ The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using the DZP-DKH basis sets^{6–9} for all atoms. The topological analysis of the electron density distribution has been performed by using the Multiwfn program (version 3.7).¹⁰

§7. Temperature dependent excitation spectra of **1**·CH₂Cl₂ and **2**

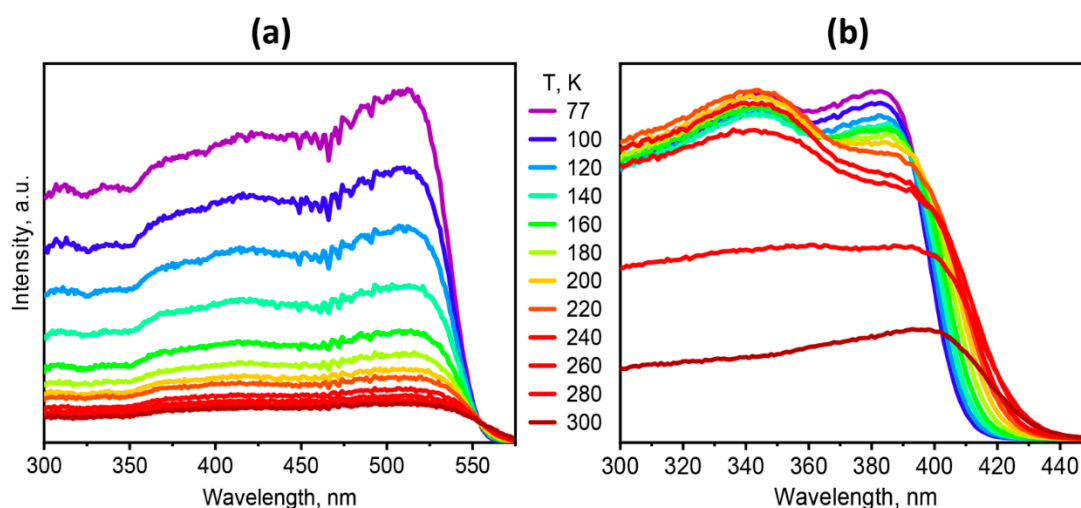


Figure S16. Temperature dependent excitation spectra of **1**·CH₂Cl₂ (a) and **2** (b) recorded at $\lambda_{\text{reg}} = 595$ and 520 nm, respectively.

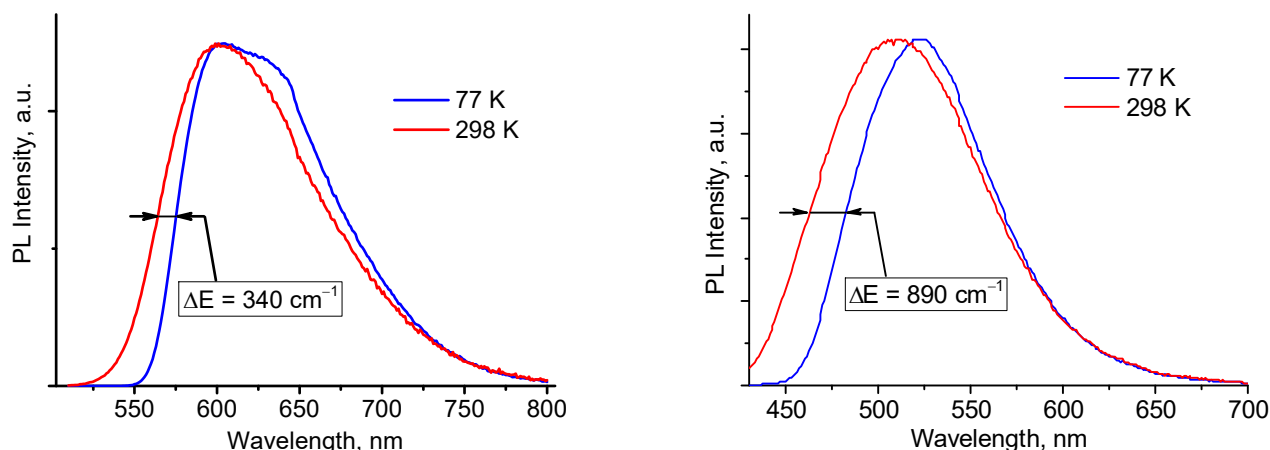


Figure S17. Red-shifting emission profile of **1**·CH₂Cl₂ (left) and **2** (right) upon cooling from 298 to 77 K.

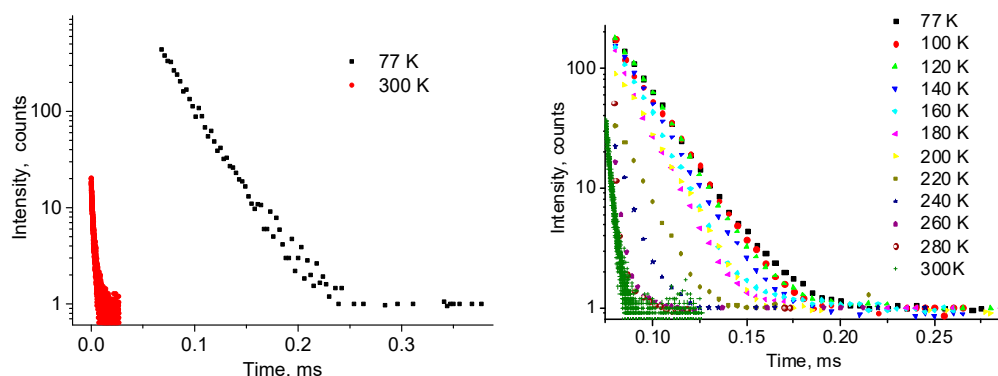


Figure S18. PL decay kinetics for **1**·CH₂Cl₂ (left) and **2** (right).

§8. References

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