

## SUPPLEMENTARY MATERIALS

### Molecular structure, vibrational spectrum and conformational properties of 4-(4-tritylphenoxy)phthalonitrile - precursor for synthesis of phthalocyanines with bulky substituent

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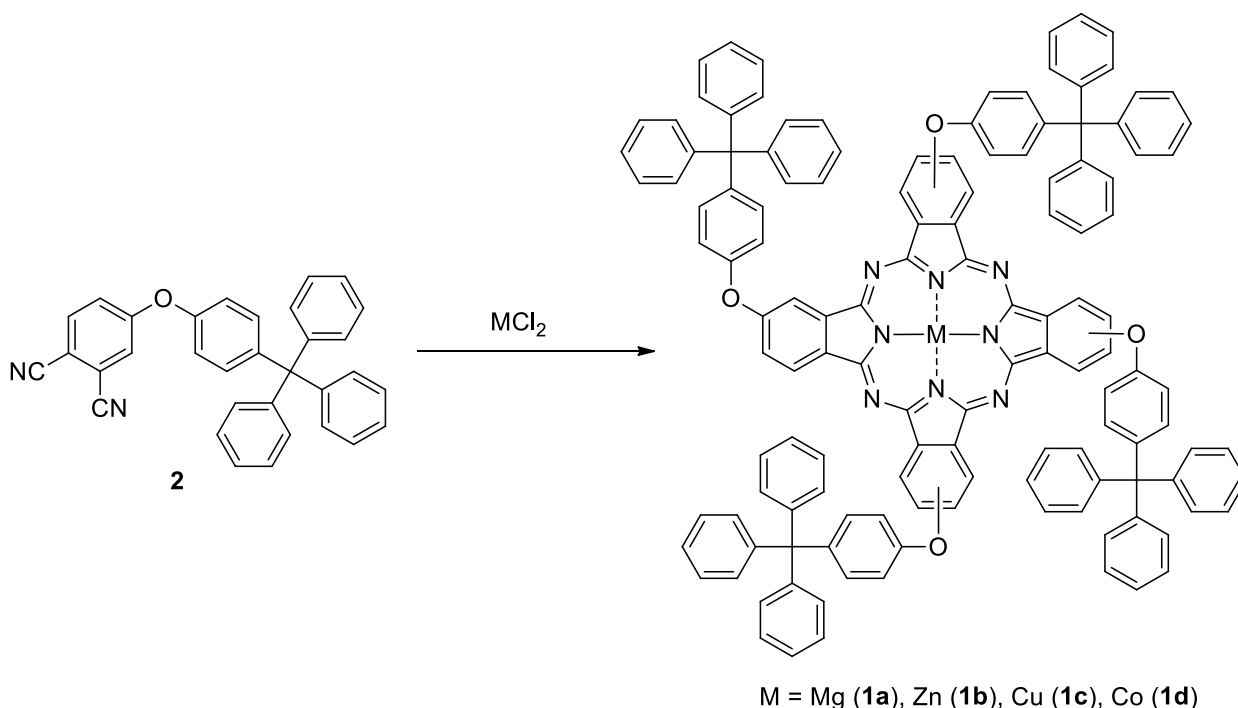
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## S1. Synthesis details

### S1-1. Introduction

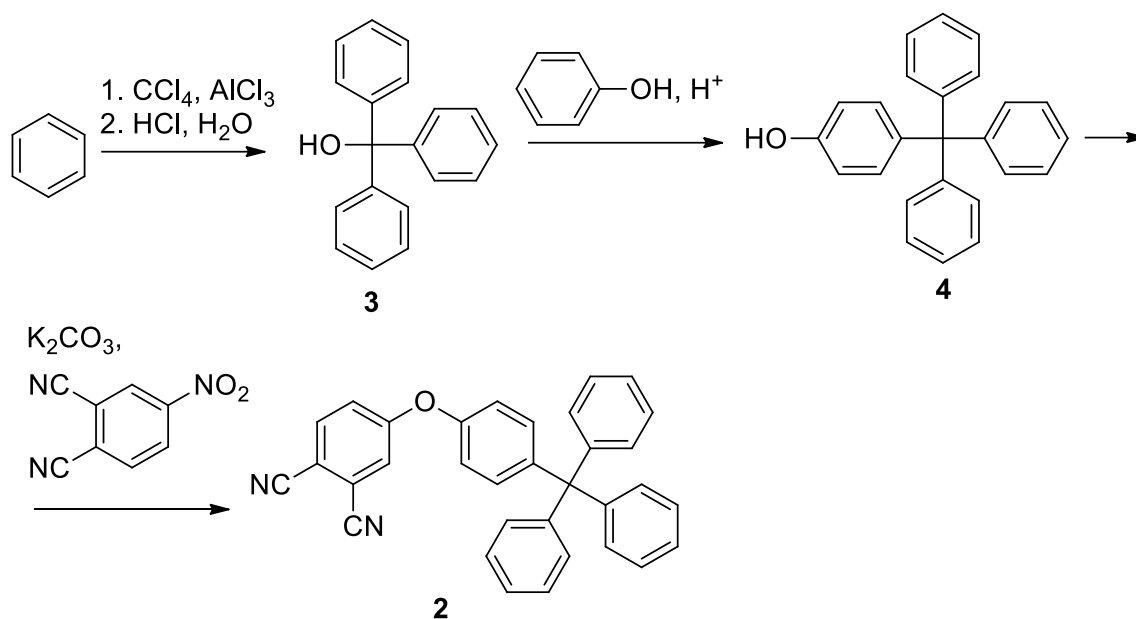
Among the huge number of phthalocyanines synthesized to date, a special place is occupied by compounds containing trityl groups in their composition. Such phthalocyanines include, among others, 2(3),9(10),16(17),23(24)-tetrakis-(4-tritylphenoxy)phthalocyanine and its complexes with various metals (**1a–1d**). *Scheme 1-1*.



*Scheme 1-1.*

The presence of bulky trityl groups in phthalocyanine and its complexes determines their liquid-crystal properties [1–4]; in addition, these compounds are promising for use in thin-film electronics [5].

The starting compound for the synthesis of phthalocyanines of group (**1**) is 4-(4-tritylphenoxy)phthalonitrile **2**. Here we present the full cycle of its synthesis, consisting of the steps of benzene alkylation with carbon tetrachloride, phenol alkylation with triphenylmethanol, and nucleophilic substitution of the nitro group in 4-nitrophthalonitrile with the 4-tritylphenol. The scheme of chemical transformations is shown in *Scheme SI-2*.



*Scheme S1-2. Synthesis of 4-(4-tritylphenoxy)phthalonitrile **2**.*

The first step in the synthesis is the alkylation of benzene. It is taken in a significant excess relative to carbon tetrachloride to maintain the mobility of the reaction mass. Alkylation yields triphenylchloromethane, which is then hydrolyzed to triphenylmethanol **3** by refluxing with hydrochloric acid. Its yield is about 60%. The unreacted benzene can be distilled off, dried, and reused in the synthesis. At the second stage, alcohol **3** is used for phenol alkylation. The reaction is carried out in an acetic acid medium catalyzed by sulfuric acid; as a result, 4-tritylphenol **4** is formed with a yield of 56%. At the third stage, phenol **4** reacts with 4-nitrophthalonitrile to form target 4-(4-tritylphenoxy)phthalonitrile **2** in 89% yield. The total yield of nitrile **2**, based on the starting carbon tetrachloride, was about 30%. The moderate yield is offset by the availability and low cost of reagents. The composition and structure of compounds **2** – **4** were confirmed by elemental analysis, mass spectra and  $^1\text{H}$  NMR spectra. In addition,  $^{13}\text{C}$  NMR spectrum.

## **S1-2. Experimental section**

### *S1-2.1. Materials and measurements*

Chloroform, tetrachloromethane and benzene of chemical grade by EKOS (<http://www.ekos-1.ru>) were used without further purification. 4-Nitrophthalonitrile were purchased from Aldrich ([www.sigmaaldrich.com](http://www.sigmaaldrich.com)). The silica-gel 60 (0.063–0.200 mm) were from Merck ([www.merck.de](http://www.merck.de)).

Mass spectroscopy measurements in both LDI-TOF (matrix-free) modes were performed with a Shimadzu AXIMA Confidence spectrometer.  $^1\text{H}$  NMR (500.13 MHz) and  $^{13}\text{C}$  NMR (125 MHz) spectra were recorded on a Bruker Avance-500 spectrometer in  $\text{CDCl}_3$ . Spectra were referenced internally by using the residual solvent resonance ( $\delta = 7.28$  ( $^1\text{H}$ ) and 77.09 ( $^{13}\text{C}$ ) ppm for  $\text{CDCl}_3$ ) relative to  $\text{SiMe}_4$  (TMS). Elemental analyses were performed on an FlashEA 1112 CHNS–O elemental analyzer. The infrared spectra were recorded for the films deposited from solution on the KRS-5 slides in the range of 400–4000  $\text{cm}^{-1}$  using an Avatar 360 FT-IR spectrometer.

#### *SI-2.2. Synthesis of triphenylmethanol (3).*

To a mixture of 100.0 g (1.28 mol) of dry benzene and 20.0 g (0.13 mol) of dry carbon tetrachloride was added 20.0 g (0.15 mol) of anhydrous aluminum chloride at room temperature in portions of 5 g over an hour, heated to boiling and kept for another 6 h, after to which 100 ml of 10% hydrochloric acid was added and stirred at the boil for 1 h. The organic layer was separated, benzene and carbon tetrachloride that did not enter into the reaction were distilled off, the residue was recrystallized from propan-2-ol. Yield 20.0 g (58%). White substance, soluble in chloroform, benzene, DMSO. MS (LDI–TOF, negative mode):  $m/z$  259.35 [Calc. for  $[M-\text{H}]^-$ : 259.12]. Another peak:  $m/z$  243.35  $[M-\text{OH}]^-$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), ppm: 7.43–7.33 (m, 15H, Ar–H), 3.01 s (1H, O–H). Anal. Calc. (%) for  $\text{C}_{19}\text{H}_{16}\text{O}$ : C 87.66, H 6.19. found: C 87.22, H 6.33.

#### *SI-2.3. Synthesis of 4-tritylphenol (4).*

A mixture of 16.0 g (0.06 mol) of compound 3 and 7.0 g (0.07 mol) of phenol was dissolved in 30 ml of acetic acid, 3 ml of concentrated sulfuric acid was added, and refluxed for 10 h. 10% sodium hydroxide solution, 200 ml water, 20 ml acetone, then recrystallized from propan-2-ol. Yield 11.6 g (56%). White substance, soluble in chloroform, benzene, DMSO. MS (LDI–TOF, negative mode):  $m/z$  335.48 [Calc. for  $[M-\text{H}]^-$ : 335.15].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), ppm: 7.29–7.26 (m, 6H, Ar–H), 7.23–7.20 (m, 9H, Ar–H), 7.10 (d, 2H,  $J=8.9$  Hz, Ar–H), 6.75 (d, 2H,  $J=8.8$  Hz, Ar–H), 4.72 (br, 1H, O–H). Anal. Calc. (%) for  $\text{C}_{25}\text{H}_{20}\text{O}$ : C 89.25, H 5.99. found: C 89.21, H 6.04.

#### *SI-2.4. Synthesis of 4-(4-tritylphenoxy)phthalonitrile (2).*

A mixture of 2.6 g (0.015 mol) of 4-nitrophthalonitrile, 6.9 g (0.02 mol) of compound **4**, 3.0 g of K<sub>2</sub>CO<sub>3</sub>, and 50 ml of DMF was stirred for 10 h at 110°C, cooled, and poured into 300 ml of water. The precipitate was filtered off, washed with 200 ml of water, dried in air at 80°C, and recrystallized from propan-2-ol. Yield 6.2 g (89%), light yellow substance, soluble in chloroform, benzene, DMSO. R<sub>f</sub> 0.59 (chloroform, Silufol). MS (LDI–TOF, negative mode): m/z 461.96 [Calc. for [M]<sup>−</sup>: 462.17]. <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm: 7.77 (d, 1H, J=8.7 Hz, Ar–H), 7.37–7.26 (m, 19H, Ar–H), 7.00 (d, 2H, J=8.6 Hz, Ar–H). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm: 161.56, 151.50, 146.35, 145.12, 135.46, 133.36, 131.04, 127.73, 126.26, 121.63, 119.35, 117.66, 115.05, 108.92, 64.67. FT–IR spectrum (ν, cm<sup>−1</sup>): 3057(C–H), 2231(C≡N), 1593(C=C), 1566, 1491, 1311, 1249 (Ar–O–Ar), 1213, 1176, 753, 704, 632. Anal. Calc. (%) for C<sub>33</sub>H<sub>22</sub>N<sub>2</sub>O: C 85.68, H 4.80, N 6.06. found: C 85.77, H 4.91, N 5.99.

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**Table S1.** Selected characteristics of 4-(4-tritylphenoxy)phthalonitrile molecule according to DFT calculations<sup>1</sup>

	B97D/cc-pVTZ				CAM-B3LYP/cc-pVTZ				PBE/cc-pVTZ			
	<i>conformer</i>				<i>conformer</i>				<i>conformer</i>			
	I	II	III	IV	I	II	III	IV	I	II	III	IV
$\Delta E_{\text{total}}$ , kcal/mol	0.428	0	0.828	0.496	0.122	0	0.345	0.266	0.129	0	0.371	0.308
$E_{\text{HOMO}}$ , eV	-5.82	-5.84	-5.90	-5.90	-8.16	-8.16	-8.26	-8.23	-6.99	-6.99	-7.09	-7.06
$E_{\text{LUMO}}$ , eV	-2.95	-2.91	-2.92	-2.88	-1.13	-1.11	-1.04	-1.03	-2.21	-2.20	-2.13	-2.13
$\mu$ , D	8.18	7.72	9.92	10.02	8.04	7.97	9.98	9.98	8.09	8.04	10.05	10.04
Parameters of a distorted tetrahedron CC <sub>4</sub> built from carbon atoms of four phenyl fragments												
C-C <sup>2</sup>	1.548	1.548	1.548	1.549	1.546	1.546	1.546	1.546	1.542	1.542	1.542	1.542
C-C-C <sup>3</sup>	113.3	113.4	113.3	113.3	111.4	111.5	111.3	111.5	111.3	111.5	111.2	111.4
C-C-C <sup>4</sup>	102.0	102.0	102.0	102.0	105.6	105.4	105.9	105.5	106.0	105.6	106.0	105.7
Parameters of Ph-O-PhN moiety												
C <sub>Ph</sub> -O	1.403	1.404	1.400	1.401	1.389	1.389	1.388	1.388	1.386	1.386	1.385	1.385
O-C <sub>PhN</sub>	1.364	1.365	1.364	1.365	1.352	1.352	1.352	1.353	1.350	1.350	1.350	1.350
C-C <sup>5</sup>	1.397	1.396	1.397	1.397	1.385	1.385	1.385	1.385	1.387	1.387	1.388	1.387
C-C <sup>6</sup>	1.403	1.404	1.403	1.403	1.388	1.388	1.388	1.388	1.392	1.392	1.391	1.391
C <sub>8</sub> -C <sub>9</sub> <sup>2</sup>	1.428	1.428	1.428	1.428	1.429	1.429	1.429	1.429	1.425	1.425	1.425	1.425
C $\equiv$ N	1.163	1.163	1.163	1.163	1.145	1.145	1.145	1.145	1.152	1.152	1.152	1.152
C <sub>PhN</sub> -O-C <sub>Ph</sub>	118.7	117.6	119.8	118.8	119.9	119.8	120.0	120.0	119.2	119.2	119.5	119.4
C-C-C <sup>5</sup>	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
C-C-C <sup>6</sup>	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
Parameters of trityl group												
C-C <sup>7</sup>	1.398	1.399	1.398	1.398	1.386	1.386	1.386	1.386	1.389	1.389	1.389	1.389
C-C <sup>7</sup>	1.399	1.399	1.399	1.399	1.386	1.386	1.386	1.386	1.389	1.389	1.389	1.389
C-C <sup>7</sup>	1.399	1.399	1.399	1.399	1.386	1.386	1.386	1.386	1.389	1.389	1.389	1.389
C-C-C <sup>7</sup>	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
C-C-C <sup>7</sup>	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
C-C-C <sup>7</sup>	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0

<sup>1</sup> distances in Å, bond angles in deg.; see Fig. 1 for numbering atoms, <sup>2</sup> averaged, <sup>3</sup> averaged value of four angles, <sup>4</sup> averaged value of two angles, <sup>5</sup> the average value in the PhO fragment, <sup>6</sup> the average value in the PhN fragment, <sup>7</sup> the average value in the phenyl ring

**Table S2.** Relative Gibbs energies ( $\Delta G^0_{478}$ , kcal/mol), and molar fractions  $\chi_i$  of conformers (mol%) in saturated vapor calculated for T=478K according to DFT calculations<sup>1</sup>

	I-IV forms	$\Delta G^0_{478}$	$\chi_i$		I-IV forms	$\Delta G^0_{478}$	$\chi_i$
B3LYP	I	0.28	29.1	CAM- B3LYP	I		27.3
	II	0.76	17.6		II	0.65	18.9
	III	0.95	14.3		III	0.80	16.2
	IV	0.0	39.0		IV	0.0	37.6
B97D	I	0.0	39.5	PBE	I	0.69	21.6
	II	0.74	18.1		II	0.85	18.4
	III	1.46	8.5		III	1.04	15.0
	IV	0.15	33.9		IV	0.0	45.0

<sup>1</sup> basis set cc-pVTZ

**Table S3.** Theoretical ( $\omega_{\text{theor}}$ ) vibrations frequencies of conformers and experimental ( $\nu_{\text{exp}}$ ) of 4-(4-tritylphenoxy)phthalonitrile. No scaled theoretical frequencies are given.

Symmetry	$\omega_{\text{theor}}, \text{cm}^{-1}$				$\nu_{\text{exp}}, \text{cm}^{-1}$	Normal vibrational energy distribution in internal coordinates for <i>cis</i> -conformer II
	I	II	III	IV		
A	3224	3224	3217	3218		$\nu(\text{C}_{\text{PhN}}\text{-H})$
A	3218	3218	3217	3217		$\nu(\text{C}_{\text{Ph}}\text{-H})$
A	3215	3214	3215	3214	3083.84	$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3215	3214	3214	3214		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3212	3211	3213	3213		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3210	3210	3213	3211		$\nu(\text{C}_{\text{PhN}}\text{-H})$
A	3198	3198	3199	3199		$\nu(\text{C}_{\text{Ph}}\text{-H})$
A	3197	3197	3197	3198		$\nu(\text{C}_{\text{PhN}}\text{-H})$
A	3192	3193	3193	3192		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3192	3192	3192	3192		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3192	3191	3191	3191		$\nu(\text{C}_{\text{thr}}\text{-H}), \nu(\text{C}_{\text{Ph}}\text{-H})$
A	3190	3190	3190	3190		$\nu(\text{C}_{\text{Ph}}\text{-H})_{\text{Ph}}, \nu(\text{C}_{\text{thr}}\text{-H})$
A	3185	3185	3185	3184	3056.83	$\nu(\text{C}_{\text{thr}}\text{-H}), \nu(\text{C}_{\text{Ph}}\text{-H})$
A	3184	3183	3183	3183		$\nu(\text{C-H})_{\text{Ph}}, \nu(\text{C}_{\text{thr}}\text{-H})$
A	3183	3183	3183	3183		$\nu(\text{C}_{\text{thr}}\text{-H}), \nu(\text{C}_{\text{Ph}}\text{-H})$
A	3183	3183	3182	3181		$\nu(\text{C}_{\text{thr}}\text{-H}), \nu(\text{C}_{\text{Ph}}\text{-H})_{\text{Ph}}$
A	3174	3173	3173	3173		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3172	3172	3172	3172		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3172	3172	3172	3171		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3165	3165	3164	3164		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3164	3164	3164	3164		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	3164	3164	3163	3163		$\nu(\text{C}_{\text{thr}}\text{-H})$
A	2344	2344	2345	2345		$\nu(\text{N-C}_{\text{N}}), \nu(\text{C}_{\text{PhN}}\text{-C}_{\text{N}})$
A	2338	2338	2338	2338	2233.25	$\nu(\text{N-C}_{\text{N}}), \nu(\text{C}_{\text{PhN}}\text{-C}_{\text{N}})$
A	1649	1649	1651	1650		$\nu(\text{C-C})_{\text{ring-all}}, \delta(\text{CCC})_{\text{ring-all}}, \delta(\text{CCH})_{\text{ring-all}}$
A	1644	1644	1645	1645		$\nu(\text{C}_{\text{Ph}}\text{-C}_{\text{Ph}})_{\text{ring}}, \nu(\text{C}_{\text{thr}}\text{-C}_{\text{thr}})_{\text{ring}}, \delta(\text{CCC})_{\text{ring-all}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{H})$
A	1640	1641	1641	1641		$\nu(\text{C}_{\text{thr}}\text{-C}_{\text{thr}})_{\text{ring}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{C}_{\text{thr}})_{\text{ring}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{H})$
A	1640	1640	1640	1640		$\nu(\text{C}_{\text{thr}}\text{-C}_{\text{thr}})_{\text{ring}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{C}_{\text{thr}})_{\text{ring}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{H})$
A	1631	1631	1633	1633	1592.9	$\nu(\text{C}_{\text{PhN}}\text{-C}_{\text{PhN}})_{\text{ring}}, \nu(\text{C}_{\text{Ph}}\text{-C}_{\text{Ph}})_{\text{ring}}, \delta(\text{OC}_{\text{PhN}}\text{C}_{\text{PhN}}), \delta(\text{CCC})_{\text{ring-all}}, \delta(\text{CCH})_{\text{ring-all}}$
A	1626	1626	1626	1626		$\nu(\text{C}_{\text{thr}}\text{-C}_{\text{thr}})_{\text{ring}}, \nu(\text{C}_{\text{Ph}}\text{-C}_{\text{Ph}})_{\text{ring}}, \delta(\text{CCC})_{\text{ring-all}}, \delta(\text{CCH})_{\text{ring-all}}$
A	1621	1621	1621	1621		$\nu(\text{C}_{\text{thr}}\text{-C}_{\text{thr}})_{\text{ring}}, \delta(\text{CCC})_{\text{C4}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{C}_{\text{thr}})_{\text{ring}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{H})$
A	1621	1621	1621	1621		$\nu(\text{C}_{\text{Ph}}\text{-C}_{\text{Ph}})_{\text{ring}}, \nu(\text{C}_{\text{thr}}\text{-C}_{\text{thr}})_{\text{ring}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{C}_{\text{thr}})_{\text{ring}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{H}), \delta(\text{C}_{\text{Ph}}\text{C}_{\text{Ph}}\text{C}_{\text{Ph}})_{\text{ring}}, \delta(\text{C}_{\text{Ph}}\text{C}_{\text{Ph}}\text{H})$
A	1620	1619	1620	1619		$\nu(\text{C}_{\text{Ph}}\text{-C}_{\text{Ph}})_{\text{ring}}, \nu(\text{C}_{\text{thr}}\text{-C}_{\text{thr}})_{\text{ring}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{C}_{\text{thr}})_{\text{ring}}, \delta(\text{C}_{\text{thr}}\text{C}_{\text{thr}}\text{H}), \delta(\text{C}_{\text{Ph}}\text{C}_{\text{Ph}}\text{C}_{\text{Ph}})_{\text{ring}}, \delta(\text{C}_{\text{Ph}}\text{C}_{\text{Ph}}\text{H}), \delta(\text{OC}_{\text{Ph}}\text{C}_{\text{Ph}})$
A	1596	1596	1593	1593		$\nu(\text{C}_{\text{PhN}}\text{-C}_{\text{PhN}})_{\text{ring}}, \delta(\text{C}_{\text{Ph}}\text{C}_{\text{Ph}}\text{C}_{\text{Ph}})_{\text{ring}}, \delta(\text{C}_{\text{Ph}}\text{C}_{\text{Ph}}\text{H}),$















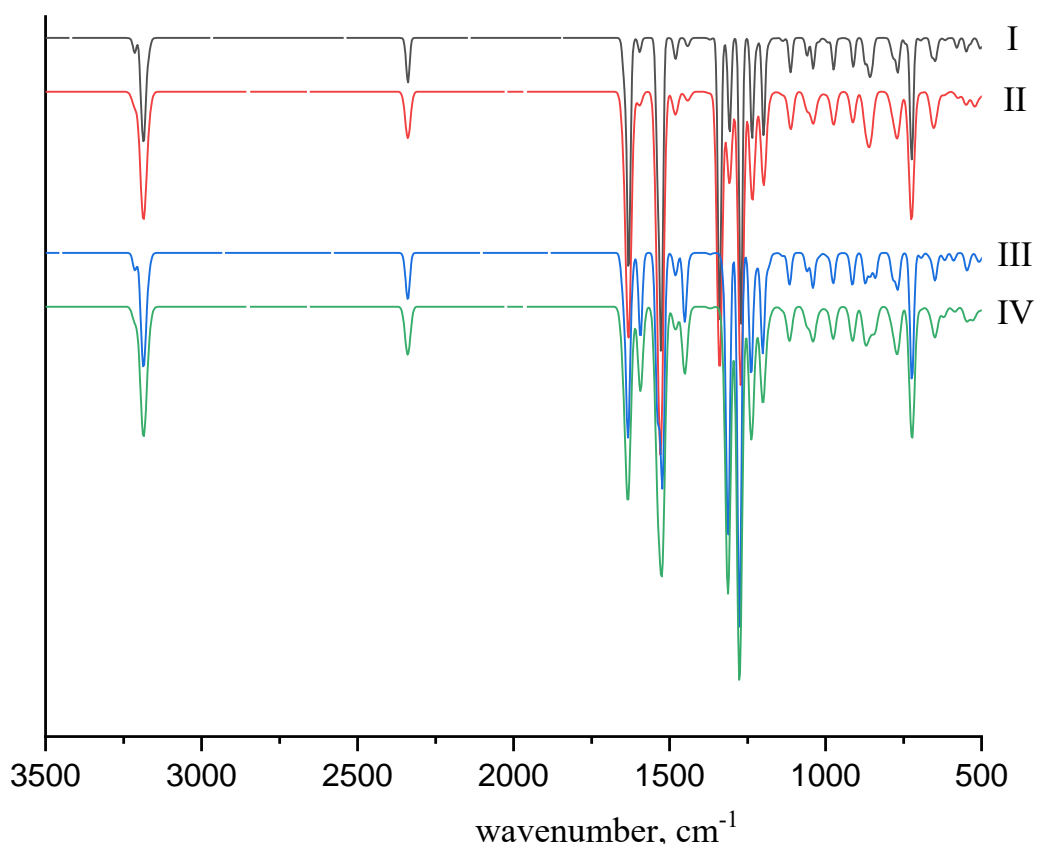




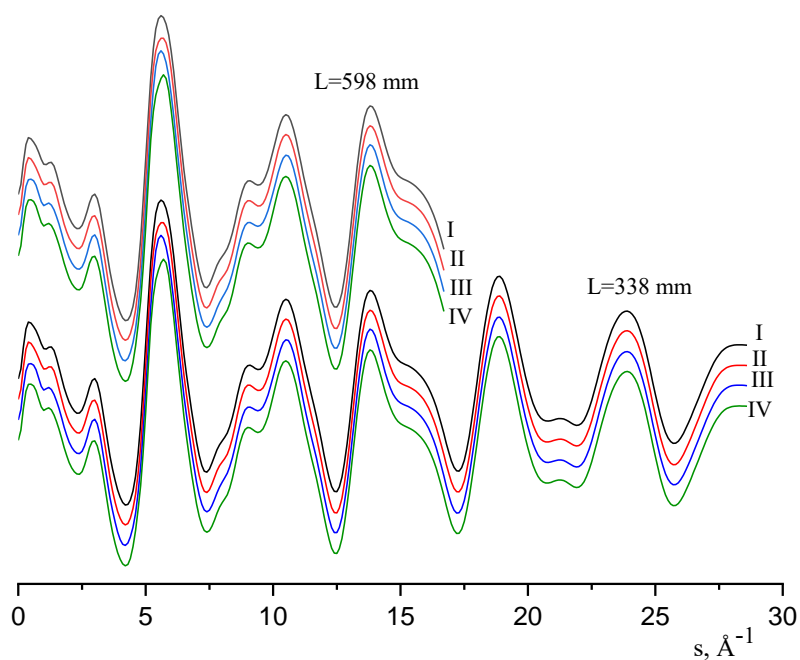




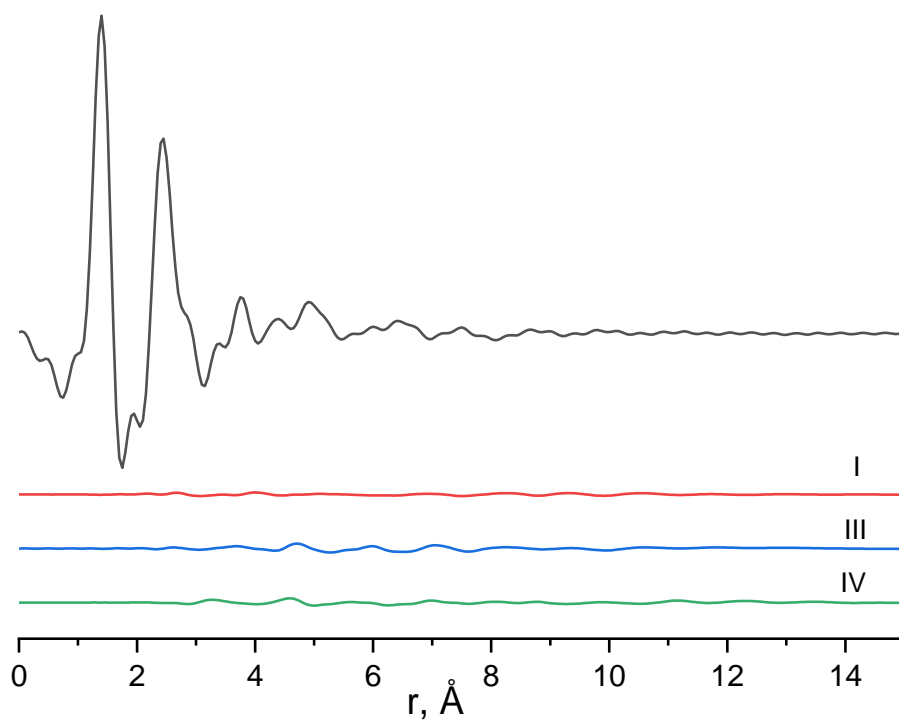




**Figure S1.** The calculated IR spectra of the conformers I and II (*cis*) and III and IV (*trans*)



**Figure S2.** Theoretical molecular intensities  $sM(s)$  of conformers I-IV of 4-(4-tritylphenoxy)phthalonitrile.



**Figure S3.** Theoretical radial distribution function  $f(r)$  for conformer II and difference  $\Delta f(r)$  for conformers I, III IV.

**Table S4.** Conditions of the synchronous GED/MS experiment.

Nozzle-to plate distances, mm	338	598
Number of recorded plates	5	6
Electron beam current, $\mu\text{A}$	1.6	1.2
Wavelength of electrons, $\text{\AA}$	0.04020(3)	0.04009(3)
Temperature of the effusion cell, K	475(10)	481(10)
Average exposure time, s	130	70
Residual gas pressure in diffraction chamber, Torr	$1.0 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$
s-range/ $\Delta s$ , $\text{\AA}^{-1}$	3.0-28.6/0.1	1.3-16.7/0.1
Ionization voltage, V	50	50