

Supplementary Information

SYNTHESIS AND PROPERTIES OF NEW 2-BENZOTHAZOLE AND 2-BENZOXAZOLE-NITROARYL-SULFIDES

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1. Experimental part (materials, instrumentation, synthesis)

1.1. Materials and instrumentation

Commercially available compounds **2a**, **2d**, **2f**, **2g** were from Aldrich; **1**, **2c**, **2e** silica gel plates 60F₂₅₄ (for TLC) and silica gel plates RP-18F_{254S} (for RP-TLC) were from Merck. Picryl chloride **2b** was prepared according to literature data.¹

¹H-NMR and ¹³C-NMR spectra were recorded with a Varian Gemini 300BB (300 MHz for ¹H and 75 MHz for ¹³C, respectively); Fourier-transform IR spectra were recorded on a Bruker Vertex 70 spectrometer with horizontal device for attenuated reflectance and diamond crystal, on a spectral window ranging from 4000 to 400 cm⁻¹. Fluorescence measurements were made with a Perkin-Elmer LS 55 spectrofluorimeter using a Xe lamp as a UV light source at ambient temperature, in the range 200-800 nm. The measurements were performed with scan speed of 200 nm×min⁻¹, slit of 10 nm, and cut-off filter of 1%. UV-Vis spectra measurements were made with a JASCO V560 spectrophotometer, in the domain 200-800 nm, with a speed of 200 nm×min⁻¹; conditions are specified in Table 1. Mass spectra were recorded with Varian 1200 L/MS/MS Triple Quadrupole with ESI interface both positive and negative ionization, fragmentation by collision with argon at 1.5 mTorr. The thermal (DSC and DTG) behavior of the compounds was followed with a Netzsch 449C STA Jupiter. Samples were placed in closed aluminum crucibles and heated with 5 K min⁻¹ from the room temperature to 200°C, under static air atmosphere. EPR spectra were recorded with a Jeol JES-FA 100 instrument. Melting points indicated below have been recorded in open capillary with Electrothermal IA 9000 Series of digital melting point instruments.

1.2. Synthesis of compounds **3a-3g**. General procedure

Starting from 2-mercaptobenzothiazole **1** and halogeno derivatives **2a-2g** (molar ratio 1:1 for **3a-3d**, **3f**, **3g** and 1:2 for **3e**) in ethanol (about 10mL/gram of **1**) and sodium hydrogen carbonate (about 1.1 mol/1 mol of **2a-2d**, **2f**, **2g** and 2.05 mol/1 mol of **2e**). The reaction mixture was refluxed: 30 minutes for **3b**, **3d**; 40 minutes for **3e**; 1 hour for **3a**, **3c**; 1 hour and 20 minutes for **3f**; 2 hours for **3g**. The precipitate was filtered off and washed with ethanol. Preparative TLC on silica gel GF₂₅₄ plates with toluene as eluent afforded the pure compounds (for **3e**, we used CH₂Cl₂:toluene=8:2 v/v).

2-(4-Nitro-2,1,3-benzoxadiazole-7-yl)-thiobenzothiazole (**3a**), 69% yield, m.p. 148-149°C for yellow crystals and 154-156°C for brick-red crystals; ESI-MS, (*m/z*); for C₁₃H₆N₄S₂O₃ (**3a**, M=330 for both type crystals), in positive: [M+H]⁺ 331; Anal.: Calcd. for C₁₃H₆N₄S₂O₃: C 47.26; H 1.83; N 16.96; S 19.41; found C 47.24; H 1.80; N 15.91; S 19.38%.

¹H-NMR (CDCl₃, δ ppm, *J* Hz, T=313K): 8.42(d, 1H, H-10, 7.8); 8.08(dd, 1H, H-4, 1.4, 7.8); 7.93(dd, 1H, H-7, 1.47.8); 7.82(d, 1H, H-9, 7.8); 7.58(td, 1H, H-6, 7.8, 1.4); 7.52(td, 1H, H-5, 7.8, 1.4)

¹³C-NMR (CDCl₃, δ ppm, T=313K): 155.93(C-2); 153.26(C-3a); 149.01 (Cq); 142.55(Cq); 136.91(Cq); 135.19(Cq); 134.42(C-1a); 130.37(C-10); 127.15(C-9); 127.11(C-6); 126.69(C-5); 123.64(C-4); 121.58(C-7).

FT-IR (ATR in solid, ν cm^{-1}): 3090w; 3052w; 2832w; 1508vs; 1418s; 1364m; 1327vs; 1160w; 1044w; 986m; 945s; 894w; 865m; 803m; 755m; 727m; 694w; 668w.

2-(2,4,6-Trinitrophenyl)thiobenzothiazole (3b), 95% yield, yellow solid, m.p. 159-161°C; ESI-MS, (m/z); for $\text{C}_{13}\text{H}_6\text{N}_4\text{S}_2\text{O}_6$ (**3b**, M=378), in positive: $[\text{M}+\text{H}]^+$ 379; Anal.: Calcd. for $\text{C}_{13}\text{H}_6\text{N}_4\text{S}_2\text{O}_6$: C 41.27; H 1.59; N 14.80; S 16.94; found C 41.24; H 1.55; N 14.77; S 17.91%.

¹H-NMR (CDCl_3 , δ ppm, J Hz, T=313K): 9.00(s, 2H, H-10, H-12); 7.81(dd, 1H, H-4, 1.5, 7.9); 7.78(dd, 1H, H-7, 1.5, 7.9); 7.45(td, 1H, H-6, 7.9, 1.5); 7.40(td, 1H, H-5, 7.9, 1.5).

¹³C-NMR (CDCl_3 , δ ppm, T=313K): 158.74(C-2); 152.31(C-3a); 151.79(C-9, C-13); 146.65(C-8); 136.07(C-11); 130.71(C-1a); 127.05(C-6); 126.18(C-5); 123.26(C-10, C-12); 122.73(C-7); 121.48(C-4).

FT-IR (ATR in solid, ν cm^{-1}): 3075m; 2970w; 1595m; 1528vs; 1455m; 1420m; 1333vs; 1238m; 1176w; 1114w; 1053w; 985m; 913m; 819w; 753m; 719m; 681w.

2-(2,4-Dinitrophenyl)thiobenzothiazole (3c), 80% yield, yellow solid, m.p. 156-157°C; ESI-MS, (m/z); for $\text{C}_{13}\text{H}_7\text{N}_3\text{S}_2\text{O}_4$ (**3c**, M=333), in positive: $[\text{M}+\text{H}]^+$ 334; Anal.: Calcd. for $\text{C}_{13}\text{H}_7\text{N}_3\text{S}_2\text{O}_4$: C 46.84; H 2.11; N 12.60; S 19.23; found C 46.82; H 2.08; N 12.55; S 19.20%.

¹H-NMR (CDCl_3 , δ ppm, J Hz, T=313K): 9.10(d, 1H, H-10, 2.1); 8.25(dd, 1H, H-12, 9.0, 2.1); 8.16(d, 1H, H-4, 7.9); 7.96(d, 1H, H-7, 7.9); 7.62(t, 1H, H-5, 7.9); 7.57(d, 1H, H-13, 9.0); 7.55(t, 1H, H-6, 7.9).

¹³C-NMR (CDCl_3 , δ ppm, T=313K): 157.49(C-2); 153.76(C-3a); 145.70(C-8); 144.99(C-9); 142.86(C-11); 137.90(C-1a); 130.21(C-6); 127.48(C-12); 127.27(C-5); 127.06(C-13); 124.19(C-4); 121.79(C-7); 121.26(C-10).

FT-IR (ATR in solid, ν cm^{-1}): 3105w; 3068w; 2923w; 2854w; 1594s; 1527s; 1454m; 1413w; 1338vs; 1308s; 1243m; 1141m; 1088m; 1043m; 985m; 920w; 898m; 830w; 761m; 724m; 673w; 604w.

2-(3,5-Dinitropyridine-2-yl)-thiobenzothiazole (3d), 60% yield, yellow solid, m.p. 200-201°C; ESI-MS, (m/z); for $\text{C}_{12}\text{H}_6\text{N}_4\text{S}_2\text{O}_4$ (**3d**, M=334), in positive: $[\text{M}+\text{H}]^+$ 335; Anal.: Calcd. for $\text{C}_{12}\text{H}_6\text{N}_4\text{S}_2\text{O}_4$: C 43.11; H 1.80; N 16.75; S 19.14; found C 43.08; H 1.77; N 16.70; S 19.10%.

¹H-NMR (CDCl_3 , δ ppm, J Hz, T=313K): 9.39(d, 1H, H-12, 2.4); 9.31(d, 1H, H-10, 2.4); 8.13(dd, 1H, H-4, 1.5, 8.0); 7.96(dd, 1H, H-7, 1.5, 8.0); 7.58(td, 1H, H-6, 8.0, 1.5); 7.52(td, 1H, H-5, 8.0, 1.5).

¹³C-NMR (CDCl_3 , δ ppm, T=313K): 161.87(C-8); 156.52(C-2); 152.75(C-3a); 141.20(C-11); 140.03(C-9); 137.74(C-1a); 147.39(C-12); 129.08(C-10); 126.78(C-6); 126.49(C-5); 123.94(C-4); 121.45(C-7).

FT-IR (ATR in solid, ν cm^{-1}): 3080m; 2921w; 2852w; 1579vs; 1539m; 1509s; 1447m; 1402m; 1325vs; 1268m; 1147m; 1117m; 1055m; 1024m; 931m; 856w; 761m; 730m; 667w; 610w.

2,2'-Bis-(2,4-dinitro-1,5-phenylene)-thiobenzothiazole (3e), 74% yield, yellow solid, m.p. 198-199°C; ESI-MS, (m/z); for $\text{C}_{20}\text{H}_{10}\text{N}_4\text{S}_4\text{O}_4$ (**3e**, M=498), in positive: $[\text{M}+\text{H}]^+$ 499; Anal.: Calcd. for $\text{C}_{20}\text{H}_{10}\text{N}_4\text{S}_4\text{O}_4$: C 48.18; H 2.02; N 11.23; S 25.72; found C 48.16, H 2.00; N 11.19, S 25.69%.

¹H-NMR (CDCl_3 , δ ppm, J Hz, T=313K): 9.19(s, H, H-10); 7.66(dd, 2H, H-4, 1.3, 7.8); 7.49(dd, 2H, H-7, 1.3, 7.8); 7.40(td, 2H, H-6, 7.8, 1.3); 7.38(s, 1H, H-13); 7.34(td, 2H, H-5, 7.8, 1.3).

¹³C-NMR (CDCl₃, δ ppm, T=313K): 156.53(C-2); 153.19(C-3a); 142.12(C-9); 141.95(C-8); 137.30(C-1a); 128.43(C-13); 127.01(C-6); 126.67(C-5); 123.73(C-4); 123.37(C-10); 121.55(C-7).

FT-IR (ATR in solid, ν cm⁻¹): 3101w; 3060w; 2991w; 1565vs; 1498s; 1447s; 1406m; 1336vs; 1309s; 1287s; 1257m; 1141m; 1084m; 1017w; 987m; 938m; 909m; 855w; 826w; 755m; 726m; 661m.

2-(2,6-Dinitro-4-trifluoromethyl-phenyl)-thiobenzothiazole (3f). 94% yield, yellow solid, m.p. 155-156°C; ESI-MS, (*m/z*); for C₁₄H₆N₃S₂O₄F₃ (**3f**, M=401), in positive: [M+H]⁺ 402; Anal.: Calcd. for C₁₄H₆N₃S₂O₄F₃: C 41.89; H 1.50; N 10.47; S 15.97; F 14.20; found C 41.86, H 1.48; N 10.42, S 15.93; F 14.15%.

¹H-NMR (CDCl₃, δ ppm, *J* Hz, T=313K): 8.43(s, 2H, H-10, H-12); 7.80(dd, 1H, H-4, 1.5, 7.7); 7.78(dd, 1H, H-7, 1.5, 7.7); 7.45(td, 1H, H-6, 7.7, 1.5); 7.38(td, 1H, H-5, 7.7, 1.5).

¹³C-NMR (CDCl₃, δ ppm, T=313K): 159.35(Cq); 152.67(Cq); 151.97(C-3a); 136.03(Cq); 132.43(q, C-11, ²*J*(¹³C-¹⁹F)=36.0 Hz); 127.26(Cq); 126.90(C-6); 125.95(C-5); 125.55(q, C-10, C-12, ³*J*(¹³C-¹⁹F)=3.7 Hz); 122.69(C-7); 121.58(q, CF₃, *J*(¹³C-¹⁹F)=274.0 Hz); 121.40(C-4).

¹⁹F-NMR (CDCl₃, δ ppm, T=313K): -68.30(s, 3F, CF₃).

FT-IR (ATR in solid, ν cm⁻¹): 3079w; 3008w; 2874w; 1620w; 1540vs; 1454w; 1424w; 1340m; 1306vs; 1242w; 1215w; 1173m; 1145vs; 1118vs; 1055w; 984m; 938m; 756m; 720m; 684w; 649w.

2-(2,4-Dinitro-6-trifluoromethyl-phenyl)-thiobenzothiazole (3g), 70% yield, yellow solid, m.p. 103-104°C; ESI-MS, (*m/z*); for C₁₄H₆N₃S₂O₄F₃ (**3g**, M=401), in positive: [M+H]⁺ 402; Anal.: Calcd. for C₁₄H₆N₃S₂O₄F₃: C 41.89; H 1.50; N 10.47; S 15.97; F 14.20; found C 41.87, H 1.47; N 10.43, S 15.92; F 14.16%.

¹H-NMR (CDCl₃, δ ppm, *J* Hz, T=313K): 8.89(d, 1H, H-12, 2.5); 8.87(d, 1H, H-10, 2.5); 7.77(dd, 1H, H-4, 1.6, 7.8); 7.76(dd, 1H, H-7, 1.6, 7.8); 7.41(td, 1H, H-6, 7.8, 1.6); 7.41(td, 1H, H-5, 7.8, 1.6).

¹³C-NMR (CDCl₃, δ ppm, T=313K): 159.82(Cq); 154.65(Cq); 152.26(C-2); 148.21(Cq); 137.45(q, C-8, ³*J*(¹³C-¹⁹F)=4.3 Hz); 135.85(Cq); 130.62 (Cq); 126.69(C-6); 125.63(C-5); 124.89(q, C-10, ³*J*(¹³C-¹⁹F)=5.8 Hz); 123.13 (C-12); 122.61(C-7); 121.47(q, CF₃, *J*(¹³C-¹⁹F)=274.5 Hz); 121.24(C-4).

¹⁹F-NMR (CDCl₃, δ ppm, T=313K): -60.23(s, 3F, CF₃).

FT-IR (ATR in solid, ν cm⁻¹): 3123w; 3085w; 2879w; 1612w; 1593w; 1541vs; 1461m; 1423m; 1342vs; 1288vs; 1151vs; 1131vs; 1108s; 1048m; 1006m; 910m; 792w; 752m; 726m; 686m.

1.3. Synthesis of compound 5. General procedure

Starting from 2-mercaptobenzoxazole **4** and NBD-Cl **2a** (molar ratio 1:1) in ethanol (about 10mL/gram of **4**) and sodium hydrogen carbonate (about 1.1mol/1 mol of **2a**). The reaction mixture was stirred at room temperature for 24 hours. The precipitate was filtered off and washed with ethanol. The product was dried and was obtained in pure state by preparative TLC using silica gel Merck GF₂₅₄ with toluene, once.

2-(4-Nitro-2,1,3-benzoxadiazole-7-yl)-thiobenzoxazole (**5**), 88% yield, yellow solid, m.p. 163.5-164.5°C; ESI-MS, (*m/z*); for C₁₃H₆N₄SO₄ (**4**, M=314), in positive: [M+H]⁺ 315; Anal.: Calcd. for C₁₃H₆N₄SO₄: C 49.68; H 1.92; N 17.82; S 10.20; found C 49.66; H 1.87; N 17.77; S 10.16%.

¹H-NMR (CDCl₃, δ ppm, *J* Hz, T=313K): 9.70(d, 1H, H-10, 8.0); 9.41(d, 1H, H-9, 8.0); 8.89(m, 1H, H-4); 8.74(m, 1H, H-7); 8.63÷8.58(m, 2H, H-5, H-6).

¹³C-NMR (CDCl₃, δ ppm, T=313K): 156.52(C-2); 151.89(C-3a); 149.55(C-11); 142.71(C-8); 141.41(C-1a); 136.16(C-12); 130.07(C-13); 130.34(C-10); 129.73(C-9); 126.30(C-6); 125.48(C-5); 120.10(C-4); 110.81(C-7).

FT-IR (ATR in solid, ν cm⁻¹): 3093m; 3037w; 1521vs; 1505vs; 1447s; 1362m; 1325vs; 1236m; 1206m; 1123m; 1091s; 1046m; 1004m; 945s; 892m; 860m; 746m730w; 672w.

2. Electronic absorption and fluorescence spectra of the synthesized compounds

2.1. Electronic absorption and fluorescence spectra of the synthesized compounds in solution

Table S1 presents the bands in visible electronic absorption spectra in five solvents. For compounds which were not dissolved completely, determination of the ε value was impossible, but we indicate the value for λ_{max}. For each solvent, the Dimroth-Reichardt empirical parameter, E_T(30),² is indicated (Table S1).

Table S1
Electronic spectral data of compounds **3a-3g** and **5**

Comp.	Solvent	E _T (30)	Conc. × 10 ⁻⁵ (M)	λ _{max} (nm)	ε × 10 ³
3a *	Toluene	33.9	2.65	403	10.09
				283	12.01
	Dichloromethane	41.1	4.05	405	11.56
				279	13.72
	Acetone	42.2	5.75	398	9.85
				407	20.72
	DMSO	45.0	3.93	281	28.59
				399	5.12
Acetonitrile	46.0	8.48	277	6.55	
			Toluene	33.9	3.71
283	11.79				
3b	Dichloromethane	41.1	2.85	398	5.05
				258	14.72
	Acetone	42.2	4.1	379	4.14
				379	4.74
	DMSO	45.0	1.45	269	19.70

Continued Table S1

Comp.	Solvent	E _T (30)	Conc. × 10 ⁻⁵ (M)	λ _{max} (nm)	ε×10 ³
3b	Acetonitrile	46.0	2.11	379	4.12
				258	15.22
3c	Toluene	33.9	-	336	-
	Dichloromethane	41.1	4.65	336	10.99
				287	10.93
	Acetone	42.2	-	326	-
	DMSO	45.0	-	335	-
	Acetonitrile	46.0	-	330	-
3d	Toluene	33.9	9.82	283	12.58
	Dichloromethane	41.1	1.94	313	10.45
				278	10.70
	Acetone	42.2	2.39	324	7.61
	DMSO	45.0	1.79	325	8.65
				279	9.24
	Acetonitrile	46.0	1.79	312	8.77
				275	8.30
				221	21.67
	3e	Toluene	33.9	1	283
Dichloromethane		41.1	0.84	313	14.10
				269	17.73
Acetone		42.2	0.92	324	21.20
DMSO		45.0	1.13	344	14.94
				271	24.89
Acetonitrile		46.0	1.44	308	13.87
				267	16.99
	224			23.88	
3f	Toluene	33.9	9.35	369	3.28
				283	10.25
	Dichloromethane	41.1	2.74	371	4.07
	Acetone	42.2	3.24	325	4.02
	DMSO	45.0	4.23	330	3.16
				270	9.00
	Acetonitrile	46.0	4.48	360	2.59
267				8.10	
3g	Toluene	33.9	9.52	283	11.22
	Dichloromethane	41.1	8.22	375	1.34
				266	8.77

Continued Table S1

Comp.	Solvent	$E_T(30)$	Conc. $\times 10^{-5}(M)$	$\lambda_{max}(nm)$	$\epsilon \times 10^3$
3g	Acetone	42.2	6.23	266	8.77
				330	3.11
	DMSO	45.0	5.23	268	14.30
				360	1.91
	Acetonitrile	46.0	1.64	266	13.92
				215	28.06
399				9.34	
5	Toluene	33.9	4.8	283	13.75
				400	9.95
	Dichloromethane	41.1	3.09	282	14.61
				391	11.13
	Acetone	42.2	4.03	280	8.4
				399	8.27
	DMSO	45.0	2.61	283	13.83
				392	9.23
	Acetonitrile	46.0	3.85	281	13.59
				273	17.09

* for brick-red crystals

2.2. In solid state

The fluorescence spectra of compounds **3a** and **5** in solid state are presented in Figure S1.

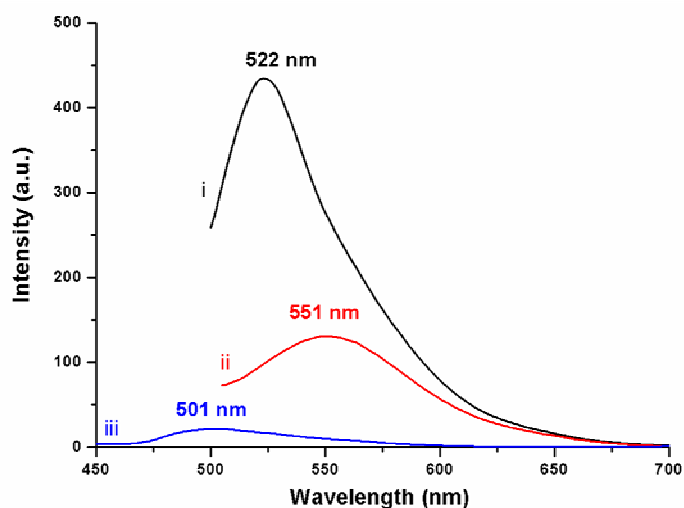


Figure S1. Fluorescence spectra in solid state (about 0.25 g), for **3a** [(i) - yellow crystal, (ii) - brick-red crystals] by excitation at 480 nm and for **5** (iii) by excitation at 373 nm

3. EPR spectra

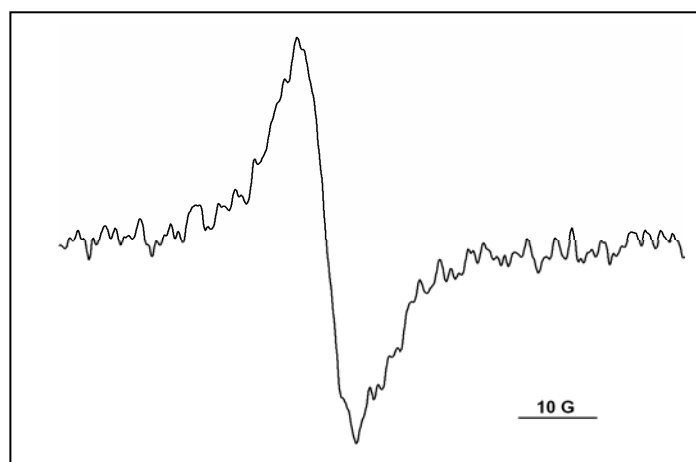


Figure S2. EPR Spectrum of **3a** (brick-red crystals) in solid state

4. Hydrophobic-hydrophilic balance

Reverse-phase thin-layer chromatography (RP-TLC) allows the determination of the molecular hydrophobicity (R_{M0})^{3,4} by plotting the relative migration distance R_f according to eqs. 1 and 2:

$$R_M = \log(1/R_f - 1) \quad 1$$

$$R_{M0} = R_M - bK \quad 2$$

where b is the slope of the R_M values versus the concentration (K) of ethanol in admixture with water. In Table S2 are presented the experimental results; the statistical parameters are: R , the correlation coefficient for R_{M0} and b (eq. 2); F , the Fisher ratio, and SD , the standard deviation.

Table S2

Experimental R_{M0} and b values,^a and calculated hydrophobicity ($M\log P$)⁵ for **3a-3g**

Comp.	Experimental values									Calcd.
	R_M in aqueous ethanol, conc.(v/v)				R_{M0}	b	Statistical parameters			$M\log P$
	80%	70%	60%	50%			R	F	SD	
3a	-0.1548	0.176	0.5284	0.7636	2.3482	-0.0310	-0.99	297.31	0.0403	2.66
3b	-0.1548	0.176	0.5284	0.7709	2.3643	-0.0313	-0.99	348.05	0.0375	3.36
3c	0.0631	0.3979	0.6843	1.0144	2.5811	-0.0314	-0.99	2295.27	0.0146	3.48
3d	-0.0377	0.2285	0.2285	0.8752	2.1037	-0.0273	-0.90	9.63	0.1973	2.06
3e	0.3297	0.7783	1.0281	1.2043	2.7029	-0.0287	-0.97	42.70	0.0983	4.14
3f	0.0126	0.3389	0.6843	1.0144	2.6905	-0.0335	-0.99	17885.02	0.0056	4.12
3g	-0.0377	0.2826	0.6419	1.0144	2.7604	-0.0351	-0.99	1729.82	0.0189	4.12
5	-0.2631	0.0246	0.3523	0.5699	2.0075	-0.0282	-0.99	341.12	0.0342	2.72

^a) Silica gel RP-18 F₂₅₄ (Merck); R_{M0} = molecular hydrophobicity; b = change in R_M value

The calculated hydrophobicity parameter $M\log P$ according to Zefirov and coworkers⁵ presents a satisfactory correlation with the experimentally determined R_{M0} value, as seen in Figure S3.

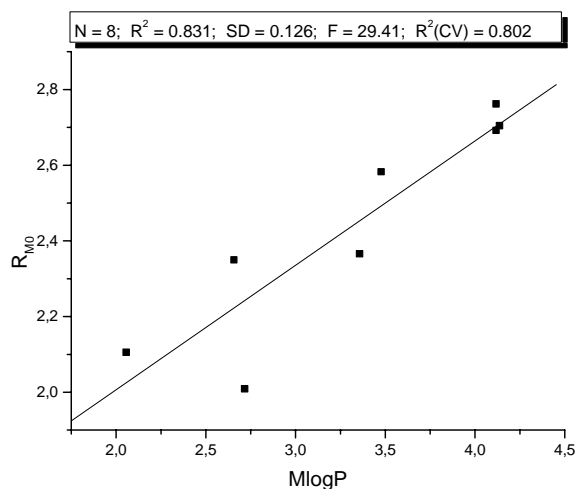


Figure S3. Plot of the molecular hydrophobicity R_{M0} versus $M\log P$

5. Crystal data and X-Ray crystallography

For compound **3a**: monoclinic, brick-red crystal (0.3 x 0.3 x 0.1 mm³), $a = 13.7650(2)$ Å, $b = 4.9564(1)$ Å, $c = 19.0550(4)$ Å, $\beta = 91.674(1)^\circ$, $V = 1299.47(1)$ Å³, space group $P 2_1/n$, $Z = 4$, $\rho = 1.689$ g.cm⁻³, μ (MoK α) = 4.29 cm⁻¹, 14168 reflections measured at 293 K on a Nonius KappaCCD diffractometer in the 2.14–28.65° θ range, 3198 unique ($R_{int}=0.026$), 199 parameters refined on F^2 using Shelxl [Sheldrick, G.M. (1997). SHELXL97. Program for the refinement of crystal structures. Univ. of Göttingen, Germany] to final indices $R[F^2 > 4\sigma F^2 : 2839 \text{ refl.}] = 0.0316$, $wR[w=1/[\sigma^2(F_o^2)+(0.0365P)^2+0.529P]]$ where $P=(F_o^2+2F_c^2)/3 = 0.0841$.

For the crystal packing of **3a** brick-red crystals, see Figure S4.

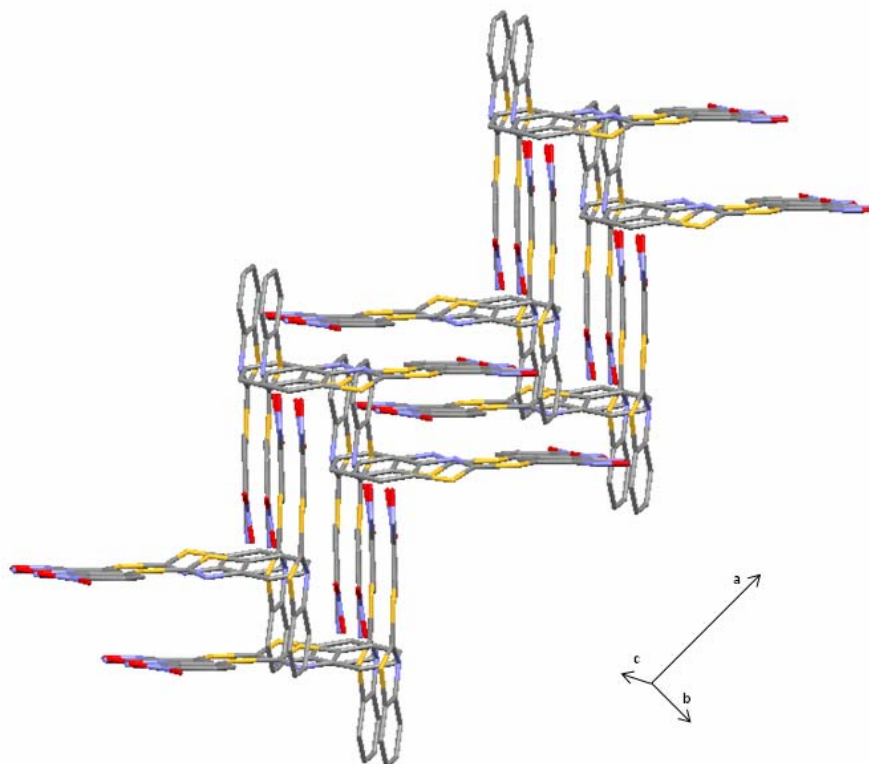


Figure S4. Crystal packing of **3a** brick-red crystals. Sulfur atoms are shaded in yellow, oxygen in red, nitrogen in blue and carbon in gray

6. Calculations

Table S3

The results of calculation for the excitation energy and oscillator strength (f) values⁶
for the compounds **3a-3g** and **5**

Comp..	Excited	Symmetry	Excitation energy (eV)	Oscillator strengths (f)
3a	1	SINGLET-A ^{''}	3.9186	0.0000
	Orbital composition:		0.297Ψ _{76→85} - 0.282Ψ _{76→86} + 0.403Ψ _{76→87} - 0.223Ψ _{76→91} + +0.151Ψ _{77→85} - 0.135Ψ _{77→86} + 0.193Ψ _{77→87} - 0.104Ψ _{77→91}	
	2	SINGLET-A ^{''}	4.1840	0.0001
	Orbital composition:		0.129Ψ _{75→87} - 0.142Ψ _{76→85} + 0.130Ψ _{76→86} - 0.186Ψ _{76→87} + +0.320Ψ _{77→85} - 0.269Ψ _{77→86} + 0.386Ψ _{77→87} - 0.198Ψ _{77→91}	
	3	SINGLET-A [']	5.153	0.9381
	Orbital composition:		0.288Ψ _{81→85} - 0.226Ψ _{83→85} + 0.568Ψ _{84→85}	
3b	1	SINGLET-A ^{''}	3.6240	0.0000
	Orbital composition:		0.145Ψ _{80→98} + 0.137Ψ _{80→99} + 0.117Ψ _{80→103} - 0.207Ψ _{82→98} - -0.194Ψ _{82→99} - 0.164Ψ _{82→103} + 0.106Ψ _{85→98} - 0.152Ψ _{87→98} - 0.142Ψ _{87→99} - 0.119Ψ _{87→103} -	
	2	SINGLET-A ^{''}	4.0320	0.0000
	Orbital composition:		-0.365Ψ _{83→97} + 0.236Ψ _{83→98} - 0.426Ψ _{83→99} - 0.175Ψ _{83→102} + +0.266Ψ _{83→103}	
	3	SINGLET-A [']	4.0804	0.0000
	Orbital composition:		0.244Ψ _{80→97} + 0.163Ψ _{80→98} - 0.203Ψ _{80→99} + 0.185Ψ _{80→102} + +0.202Ψ _{81→97} + 0.130Ψ _{81→98} - 0.164Ψ _{81→99} + 0.151Ψ _{81→102} + 0.224Ψ _{82→97} + 0.147Ψ _{82→98} -	
3c	1	SINGLET-A ^{''}	3.8760	0.0000
	Orbital composition:		0.187Ψ _{73→86} + 0.210Ψ _{73→87} - 0.146Ψ _{73→99} - 0.145Ψ _{73→92} - -0.145Ψ _{75→86} - 0.163Ψ _{75→87} + 0.110Ψ _{75→89} + 0.111Ψ _{75→92} - 0.213Ψ _{77→86} - 0.237Ψ _{77→87} +	
	2	SINGLET-A ^{''}	4.0362	0.0000
	Orbital composition:		0.409Ψ _{74→86} - 0.383Ψ _{74→87} + 0.171Ψ _{74→88} + 0.255Ψ _{74→89} - -0.273Ψ _{74→92}	
	3	SINGLET-A [']	4.2502	0.0001
	Orbital composition:		0.261Ψ _{75→86} - 0.267Ψ _{75→87} + 0.110Ψ _{75→88} + 0.171Ψ _{75→89} - -0.163Ψ _{75→92} - 0.287Ψ _{77→86} + 0.248Ψ _{77→87} - 0.114Ψ _{77→88} - 0.159Ψ _{77→89} + 0.179Ψ _{77→92} +	
3d	1	SINGLET-A ^{''}	3.8970	0.0000
	Orbital composition:		-0.252Ψ _{73→86} - 0.267Ψ _{73→87} + 0.208Ψ _{73→89} + 0.196Ψ _{73→90} - -0.194Ψ _{76→86} - 0.207Ψ _{76→87} + 0.160Ψ _{76→89} + 0.148Ψ _{76→90} + 0.117Ψ _{77→86} + 0.118Ψ _{77→87} -	
	2	SINGLET-A ^{''}	4.2130	0.0000
	Orbital composition:		-0.156Ψ _{73→86} + 0.149Ψ _{73→87} + 0.111Ψ _{73→90} - 0.139Ψ _{75→86} + +0.126Ψ _{75→87} + 0.273Ψ _{76→86} - 0.252Ψ _{76→87} + 0.118Ψ _{76→88} + 0.162Ψ _{76→89} - 0.176Ψ _{76→90} -	
	3	SINGLET-A [']	4.2670	0.0000
	Orbital composition:			

Continued Table S3

Comp.	Excited	Symmetry	Excitation energy (eV)	Oscillator strengths (f)
3d	Orbital composition:		$0.101\Psi_{70\rightarrow86} + 0.114\Psi_{70\rightarrow87} - 0.175\Psi_{76\rightarrow86} - 0.179\Psi_{76\rightarrow87} +$	
			$+0.130\Psi_{76\rightarrow89} + 0.126\Psi_{76\rightarrow90} - 0.318\Psi_{77\rightarrow86} - 0.327\Psi_{77\rightarrow87} + 0.231\Psi_{77\rightarrow89} + 0.208\Psi_{77\rightarrow90}$	
3e	1	SINGLET-A ⁿ	4.0650	0.0010
	Orbital composition:		$0.102\Psi_{111\rightarrow128} - 0.313\Psi_{112\rightarrow123} + 0.214\Psi_{112\rightarrow129} - 0.211\Psi_{112\rightarrow130} +$	
			$+0.120\Psi_{112\rightarrow132} + 0.279\Psi_{112\rightarrow133} + 0.143\Psi_{113\rightarrow128} - 0.125\Psi_{113\rightarrow133}$	
	2	SINGLET-A ⁿ	4.1525	0.0002
	Orbital composition:		$-0.128\Psi_{111\rightarrow129} - 0.147\Psi_{111\rightarrow132} - 0.121\Psi_{112\rightarrow128} + 0.267\Psi_{114\rightarrow129} -$	
			$-0.170\Psi_{114\rightarrow130} + 0.226\Psi_{114\rightarrow132} + 0.128\Psi_{114\rightarrow133} - 0.273\Psi_{117\rightarrow128} + 0.154\Psi_{117\rightarrow131} - 0.121\Psi_{117\rightarrow132} +$	
3	SINGLET-A ⁿ	4.1623	0.0002	
Orbital composition:		$-0.111\Psi_{111\rightarrow128} - 0.125\Psi_{111\rightarrow129} + 0.103\Psi_{111\rightarrow131} - 0.149\Psi_{111\rightarrow132} -$		
		$-0.115\Psi_{112\rightarrow129} - 0.101\Psi_{112\rightarrow132} + 0.313\Psi_{114\rightarrow128} + 0.110\Psi_{114\rightarrow130} - 0.143\Psi_{114\rightarrow131} - 0.227\Psi_{114\rightarrow133} -$		
3f	1	SINGLET-A ⁿ	3.6378	0.0000
	Orbital composition:		$0.151\Psi_{88\rightarrow103} - 0.114\Psi_{88\rightarrow107} + 0.122\Psi_{90\rightarrow102} + 0.244\Psi_{90\rightarrow103} +$	
			$+0.100\Psi_{90\rightarrow105} - 0.154\Psi_{90\rightarrow106} - 0.181\Psi_{90\rightarrow107} - 0.178\Psi_{93\rightarrow103} + 0.112\Psi_{93\rightarrow106} + 0.131\Psi_{93\rightarrow107} -$	
	2	SINGLET-A ⁿ	4.0772	0.0000
	Orbital composition:		$-0.365\Psi_{88\rightarrow102} + 0.115\Psi_{88\rightarrow103} + 0.129\Psi_{88\rightarrow105} - 0.205\Psi_{88\rightarrow106} +$	
			$+0.170\Psi_{88\rightarrow107} - 0.128\Psi_{89\rightarrow102} + 0.297\Psi_{90\rightarrow102} - 0.104\Psi_{90\rightarrow105} + 0.162\Psi_{90\rightarrow106} - 0.135\Psi_{90\rightarrow107} -$	
3	SINGLET-A ⁿ	4.3370	0.0001	
Orbital composition:		$-0.138\Psi_{92\rightarrow103} - 0.206\Psi_{93\rightarrow102} - 0.392\Psi_{93\rightarrow103} - 0.151\Psi_{93\rightarrow105} +$		
		$+0.231\Psi_{93\rightarrow103} + 0.265\Psi_{93\rightarrow107} + 0.118\Psi_{95\rightarrow103} - 0.114\Psi_{99\rightarrow103}$		
3g	1	SINGLET-A ⁿ	4.0401	0.0000
	Orbital composition:		$-0.362\Psi_{90\rightarrow102} + 0.387\Psi_{90\rightarrow103} - 0.225\Psi_{90\rightarrow104} - 0.265\Psi_{90\rightarrow106} -$	
			$-0.283\Psi_{90\rightarrow107}$	
	2	SINGLET-A ⁿ	4.0804	0.0000
	Orbital composition:		$0.384\Psi_{88\rightarrow102} + 0.324\Psi_{88\rightarrow103} - 0.271\Psi_{88\rightarrow106} + 0.237\Psi_{88\rightarrow107} +$	
			$+0.163\Psi_{92\rightarrow102} + 0.137\Psi_{92\rightarrow103} - 0.112\Psi_{92\rightarrow106}$	
3	SINGLET-A ⁿ	4.2657	0.0001	
Orbital composition:		$0.102\Psi_{89\rightarrow103} + 0.211\Psi_{92\rightarrow102} - 0.224\Psi_{92\rightarrow103} + 0.126\Psi_{92\rightarrow104} +$		
		$+0.148\Psi_{92\rightarrow106} + 0.153\Psi_{92\rightarrow107} + 0.294\Psi_{93\rightarrow102} - 0.304\Psi_{93\rightarrow103} + 0.172\Psi_{93\rightarrow104} + 0.198\Psi_{93\rightarrow106} +$		
5	1	SINGLET-A ⁿ	3.9205	0.0000
	Orbital composition:		$0.302\Psi_{74\rightarrow81} + 0.471\Psi_{74\rightarrow82} + 0.153\Psi_{74\rightarrow83} - 0.221\Psi_{74\rightarrow87} - 0.153\Psi_{76\rightarrow87}$	
			$+0.223\Psi_{76\rightarrow82} - 0.103\Psi_{76\rightarrow87}$	
	2	SINGLET-A ⁿ	4.1878	0.0001
	Orbital composition:		$-0.159\Psi_{74\rightarrow81} - 0.239\Psi_{74\rightarrow82} + 0.106\Psi_{74\rightarrow87} + 0.324\Psi_{76\rightarrow81} +$	
			$+0.448\Psi_{76\rightarrow82} + 0.146\Psi_{76\rightarrow83} - 0.196\Psi_{76\rightarrow87}$	
3	SINGLET-A ⁿ	5.2603	0.8494	
Orbital composition:		$0.203\Psi_{77\rightarrow81} + 0.303\Psi_{79\rightarrow81} + 0.575\Psi_{80\rightarrow81}$		

Molecular orbitals⁶ for transition 76 \rightarrow 85 in case of compound **3a** are presented in Figure S5.

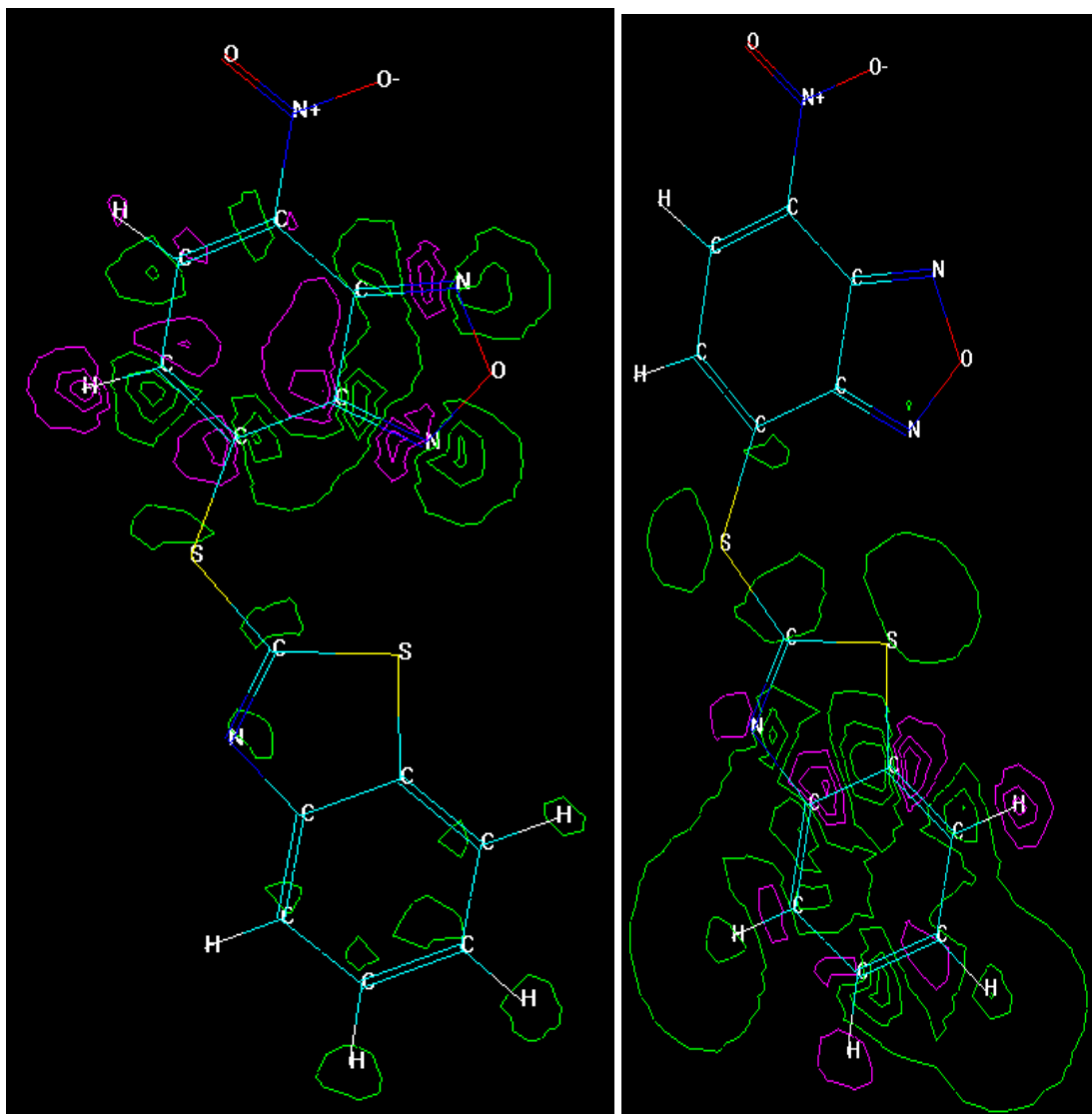


Figure S5. Molecular orbitals for transition 76 \rightarrow 85 in case of compound **3a**

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