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Electronic Supplementary Information

Supramolecular Hierarchy among Halogen and Hydrogen Bond Donors in Azopolymer Surface Patterning

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1. General information

Starting materials were purchased from Sigma-Aldrich, Acros Organics, Apollo Scientific, Polymer Source and TCI Europe, and used as received. Commercial HPLC-grade solvents were used without further purification, except for anhydrous tetrahydrofuran (THF), which was distilled over sodium/benzophenone before use.[S1] Triethylamine was distilled over calcium hydride just before use.[S1] ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at room temperature on a Bruker AV400 or AV500 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to tetramethylsilane (TMS) using the residual proton or carbon impurities of the deuterated solvents as standard reference, while ^{19}F chemical shifts were referenced to an internal $CFCl_3$ standard. Attenuated total reflectance FTIR (ATR-FTIR) spectra were obtained with a Nicolet Nexus FTIR spectrometer. The values were given in wavenumbers and were rounded to 1 cm^{-1} upon automatic assignment. Mass spectra were recorded on a BRUKER Esquire 3000 PLUS. DSC analyses were performed on a Mettler Toledo DSC823e differential scanning calorimeter, using aluminium 40 μL sample pans and Mettler STARe software for calculation. Melting points were also determined on a Reichert instrument, by observing the melting process through an Olympus BH-2 optical microscope. Elemental analyses were carried out on a Costech ECS 4010 analyzer, allowing simultaneous C, H and N quantification. Results are given as an average of three measurements.

2. Synthetic procedures

Compounds **2**, **3** and **4** were synthesized as previously reported.[S2] Dye **7** was purchased from TCI Europe. Synthesis of azobenzenes **1**, **5**, **6**, **8** and **9** is described below.

2.1. Synthesis of *N*,*N*-dimethyl-4-((pentafluorophenyl)diazenyl)aniline

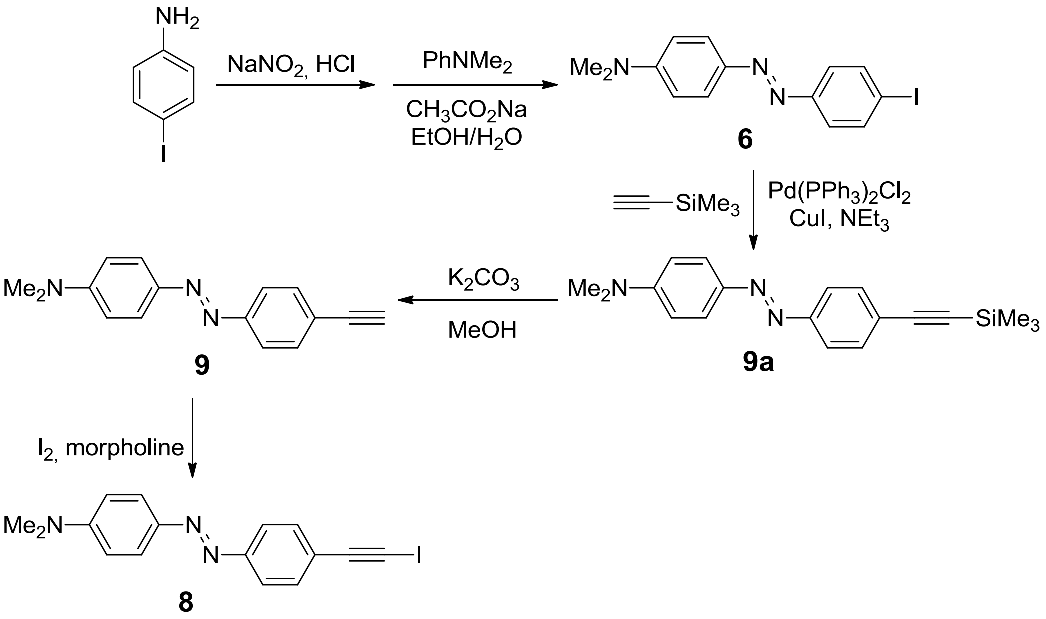
In a 100 mL round-bottom flask equipped with a stir bar, a mixture of water (40 mL) and acetone (20 mL) was set to cool in an ice bath. Once the solvent temperature was below 5 °C, pentafluoroaniline (0.55 mL, 3 mmol) was added, followed by $NaNO_2$ (0.25 g, 3.6 mmol) and concentrated HF (0.5 mL, 15 mmol). The solution was left to stir for 30 minutes, then *N*,*N*-dimethylaniline (0.38 mL, 3 mmol) was added. The solution rapidly turned deep orange, then red, and was left to react for 1 more hour. After this time, the reaction mixture was extracted with ethyl acetate (2×150 mL). Combined organic phases were washed with water (2×200 mL) and then brine (100 mL), dried over $MgSO_4$ and concentrated. The crude product was purified twice by silica gel chromatography, using a gradient of 0-40% ethyl acetate in hexane. Yield: 0.2 g (12%).

Decomposed without melting (T > 163 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.88 (d, 2H, *J* = 9.36 Hz), 6.82 (d, 2H, *J* = 9.07 Hz), 3.15 (s, 6H). **^{19}F NMR** (500 MHz, $CDCl_3$) δ: -152.4, -156.9, -163.8. **^{13}C NMR** (400 MHz, $CDCl_3$) δ: 147.9, 139.5, 106.8, 35.4 [*Note*: Carbon signals of the pentafluoro benzene ring are not present, due to C-F coupling]. **HR-MS** (APCI, 4 kV) *m/z*: Calculated for $C_{14}H_{11}F_5N_3$ $[M+H]^+$: 316.0867; found: 316.0858; $C_{14}H_{10}F_5N_3$ $[M]^-$: 315.0800; found: 315.0507.

2.2. Synthesis of (*E*)-4-((4-(dimethylamino)phenyl)diazenyl)-2,3,5,6-tetrafluorophenol (5)

Pentafluoroaniline (0.3 g, 1.6 mmol) was dissolved in 70% w/w H_2SO_4 (2 mL) and treated with sodium nitrite (0.18 g, 2.6 mmol). After stirring for 2 h, the solution was rendered alkaline by addition (over 4 h) of a solution of sodium carbonate (2.65 g) in distilled water (13 mL), keeping the temperature at 0 °C. After stirring for further 30 minutes, the mixture was acidified with 70% w/w H_2SO_4 (1 mL) and treated with *N*,*N*-dimethylaniline (2 mL, 15.8 mmol). One hour later, the orange-red precipitate was filtered off, washed with water, and dried. The filtrate was extracted two times with diethyl ether, and the combined extracts dried over anhydrous Na_2SO_4 and evaporated. The residue was than triturated and stirred with anhydrous acetic acid, filtered with a sintered glass funnel and recrystallized from methanol, to give 0.24 g (0.77 mmol, 48% yield) of **5** as orange crystals.

Decomposed without melting (T > 157 °C). **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ: 7.72 (d, 2H, J = 5 Hz), 6.83 (d, 2H, J = 5 Hz), 3.07 (s, 3H). **^{19}F NMR** (475 MHz, DMSO-*d*$_6$) δ: -155.16 (m, 2F), -163.95 (bs, 2F). **FTIR** (cm^{-1}): 2913, 1635, 1597, 1556, 1526, 1503, 1444, 1401, 1365, 1305, 1271, 1241, 1230, 1139, 1066, 1012, 945, 887, 743, 731, 718, 663, 632, 593. **MS (ESI-)** *m/z*: 312.2 [M-H]. **Anal. Calcd for $C_{14}H_{11}N_3F_4O$**: C 53.7, H 3.5, N 13.4. Found: C 53.6, H 3.4, N 13.6.



Scheme S1 Synthetic route to compounds **6**, **9** and **8**.

2.3. Synthesis of (*E*)-4-((4-iodophenyl)diazenyl)-*N*,*N*-dimethylaniline (6)

Compound **6** was prepared according to a reported procedure.[S3] In a round-bottom flask, 4-iodoaniline (2.5 g, 11 mmol) was dissolved in water (35 mL) and cooled to -5 °C, then HCl 37% (3.5 mL) was added. A solution of sodium nitrite (0.9 g, 13 mmol) in water (9 mL) was cooled to -5 °C and added dropwise to the aniline solution, under stirring. In an Erlenmeyer flask, sodium acetate (0.5 g, 6 mmol) and *N*,*N*-dimethylaniline (2.9 mL, 23 mmol) were dissolved in ethanol/water 5:2 mixture (70 mL), stirred for 20 minutes, cooled to -5 °C and then added to the previous solution. After stirring at r.t. overnight, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL), extracted with dichloromethane, dried over Na_2SO_4 and concentrated under vacuum. Purification of the crude residue by flash silica gel chromatography, eluting with hexane/ethyl acetate (95:5), afforded **6** as a bright orange solid (1.7 g, 44% yield).

m.p. 153-156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.87 (d, 2H, *J* = 9.2 Hz), 7.80 (d, 2H, *J* = 8.7 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 6.75 (d, 2H, *J* = 9.2 Hz), 3.09 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.72, 152.70, 143.62, 138.10 (2×CH), 125.18 (2×CH), 123.96 (2×CH), 111.55 (2×CH), 95.12, 40.26 (2×CH_3). **FTIR** (cm^{-1}): 2900, 2812, 1598, 1357, 1154, 819, 526. **MS (ESI+)** *m/z*: 352.0 [M+H]. **Anal. Calcd for $C_{14}H_{14}IN_3$**: C 47.88, H 4.02, N 11.97. Found: C 48.07, H 3.98, N 11.80.

2.4. Synthesis of (*E*)-*N*,*N*-dimethyl-4-((4-((trimethylsilyl)ethynyl)phenyl)diazenyl)aniline (9a)

Following a standard protocol for Sonogashira coupling,[S4] compound **6** (0.45 g, 1.3 mmol), $Pd(PPh_3)_2Cl_2$ (0.05 g, 0.07 mmol) and copper iodide (0.025 g, 0.13 mmol) were added successively to an oven-dried three-necked flask, under nitrogen. Anhydrous THF (9 mL) and triethylamine (1.6 mL, 11 mmol) were then added, finally followed by trimethylsilylacetylene (0.22 mL, 1.6 mmol). After stirring at r.t. for four hours, the reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with dichloromethane (3×35 mL). The crude was purified by flash column chromatography, using hexane/ethyl acetate (95:5) as eluent. Product **9a** (0.36 g, 87% yield) was obtained as a red solid.

m.p. 150-152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.90 (d, 2H, *J* = 9 Hz), 7.79 (d, 2H, *J* = 8.7 Hz), 7.56 (d, 2H, *J* = 8.7 Hz), 6.78 (d, 2H, *J* = 9 Hz), 3.09 (s, 6H), 0.28 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.67, 152.62, 143.76, 132.70 (2×CH), 125.16 (2×CH), 123.85, 122.10 (2×CH), 111.50 (2×CH), 105.17, 95.90, 40.25 (2×CH_3), -0.04 (3×CH_3). **FTIR** (cm^{-1}): 2971, 2900, 2171, 1601, 1367, 1132, 836, 820, 756, 556. **MS (ESI+)** *m/z*: 322.2 [M+H]. **Anal. Calcd for $C_{19}H_{23}N_3Si$**: C 70.98, H 7.21, N 13.07. Found: C 70.16, H 7.30, N 13.01.

2.5. Synthesis of (*E*)-4-((4-ethynylphenyl)diazenyl)-*N*,*N*-dimethylaniline (9)

According to a reported method,[S4] K_2CO_3 (0.14 g, 1 mmol) was added to a solution of **9a** (0.3 g, 1 mmol) in methanol (75 mL). After stirring at r.t. for four hours, the solvent was removed under vacuum and the residue was dissolved in dichloromethane (60 mL), washed with distilled water (2×50 mL) and brine (50 mL), then dried over Na_2SO_4 and concentrated. Silica gel flash chromatography with hexane/ethyl acetate (9:1) gave compound **9** (0.2 g, 80% yield) as an orange solid.

m.p. 149-152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.88 (d, 2H, *J* = 9.2 Hz), 7.80 (d, 2H, *J* = 8.5 Hz), 7.59 (d, 2H, *J* = 8.5 Hz), 6.76 (d, 2H, *J* = 9.2 Hz), 3.17 (s, 1H), 3.09 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.05, 152.75, 143.85, 132.86 (2×CH), 125.22 (2×CH), 122.81, 122.18 (2×CH), 111.57 (2×CH), 83.77, 78.46, 40.23 (2×CH_3). **FTIR** (cm^{-1}): 3275, 2896, 1600, 1362, 1135, 845, 822, 656, 626, 553. **MS (ESI+)** *m/z*: 250.1 [M+H]. **Anal. Calcd for $C_{16}H_{15}N_3$**: C 77.08, H 6.06, N 16.85. Found: C 76.63, H 6.14, N 17.45.

2.6. Synthesis of (*E*)-4-((4-(iodoethynyl)phenyl)diazenyl)-*N*,*N*-dimethylaniline (8)

Compound **8** was prepared following a slightly modified literature procedure.[S5] Iodine (0.14 g, 0.55 mmol) and morpholine (0.13 mL, 1.5 mmol) were dissolved in benzene (1.5 mL) and stirred at r.t. for 30 minutes. Then a suspension of **9** (0.125 g, 0.5 mmol) in benzene (3.5 mL) was slowly added to the previous solution and stirring was continued at 45°C for 24 hours. The final mixture was filtered and the residue was taken up with diethyl ether and acetone. Combined organic phases were washed with saturated aqueous NH_4Cl, $NaHCO_3$ and finally with water. After solvent removal, the crude was chromatographed on silica gel with hexane/dichloromethane (8:2) giving **8** as a bright orange solid (0.095 g, 51% yield).

Decomposed without melting (T > 180 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.87 (d, 2H, *J* = 9.1 Hz), 7.79 (d, 2H, *J* = 8.4 Hz), 7.53 (d, 2H, *J* = 8.4 Hz), 6.76 (d, 2H, *J* = 9.1 Hz), 3.10 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.72, 143.72, 133.09 (2×CH), 128.35, 125.38, 124.00, 122.08 (2×CH), 111.56 (2×CH), 94.31 (2×CH), 40.33 (2×CH_3), 7.80. **FTIR** (cm^{-1}): 2919, 2850, 1595, 1339, 1115, 833, 554. **MS (ESI+)** *m/z*: 376.0 [M+H]. **Anal. Calcd for $C_{16}H_{14}IN_3$**: C 51.22, H 3.76, N 11.20. Found: C 51.55, H 3.88, N 11.38.

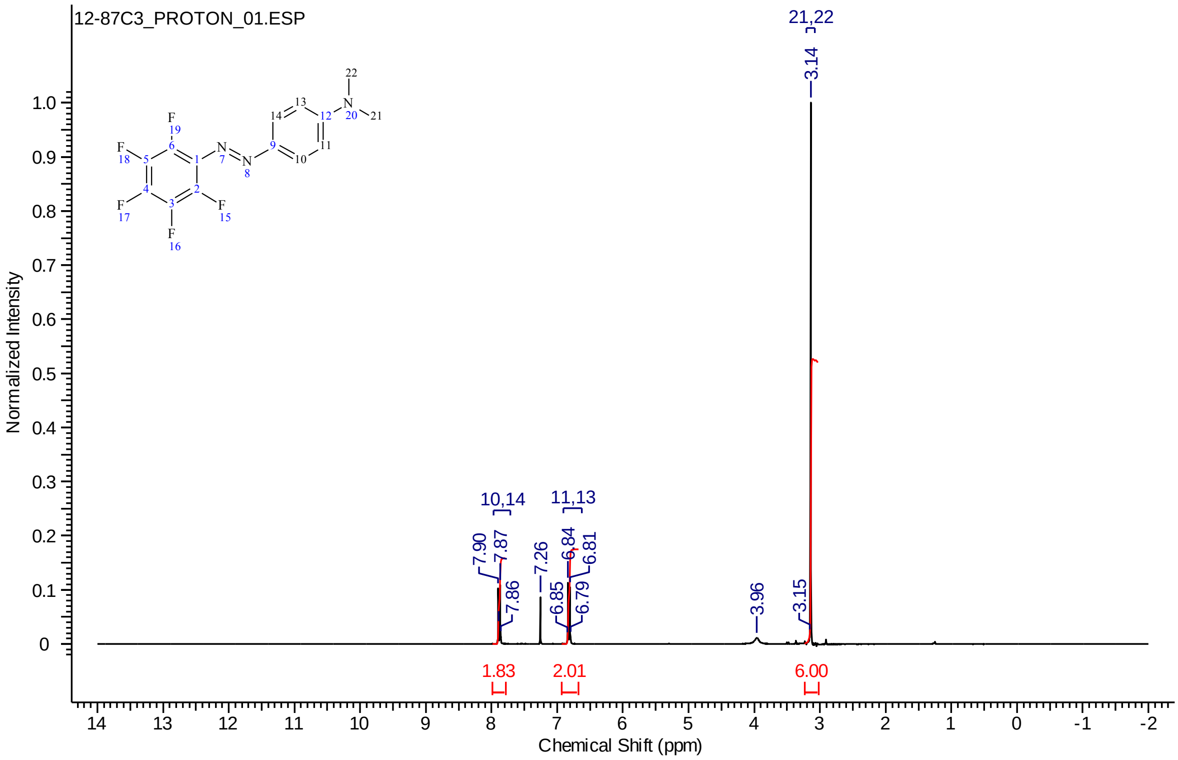


Fig. S1 ^{19}F NMR (500 MHz, CDCl$_3$, TFA standard) of compound **1**.

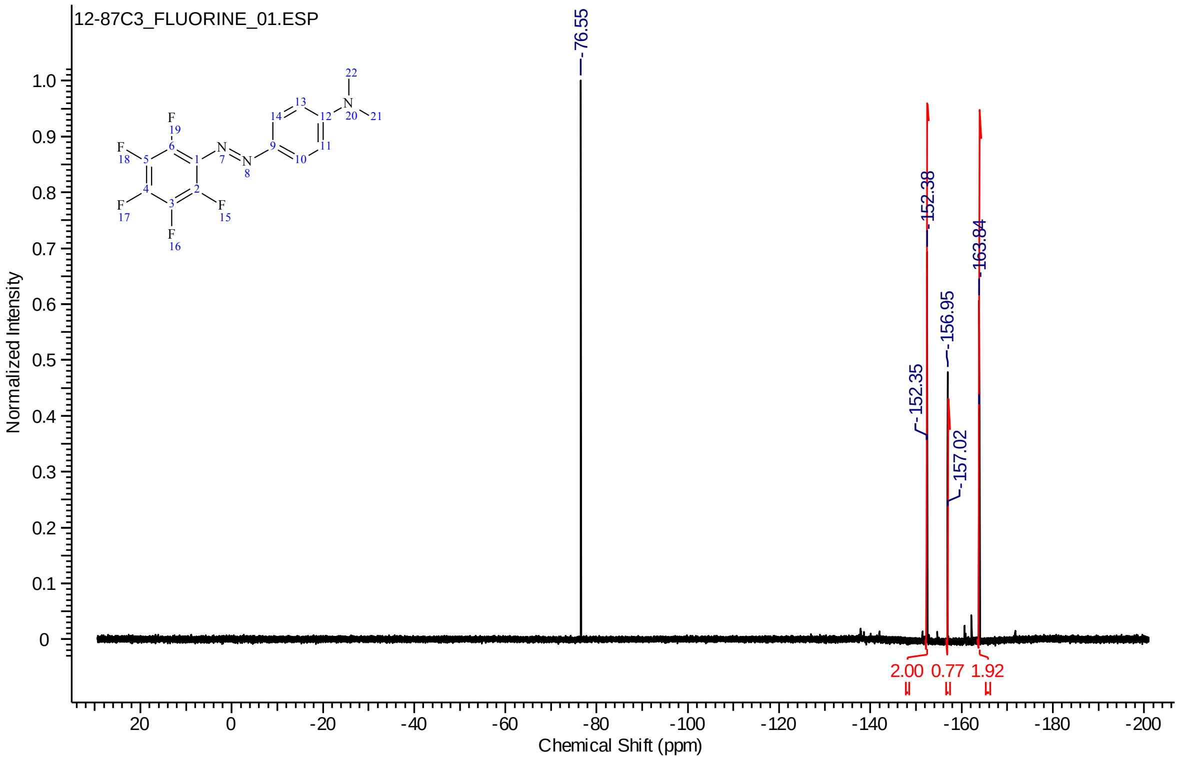


Fig. S2 ^{13}C NMR (400 MHz, CDCl$_3$) of compound **1**.

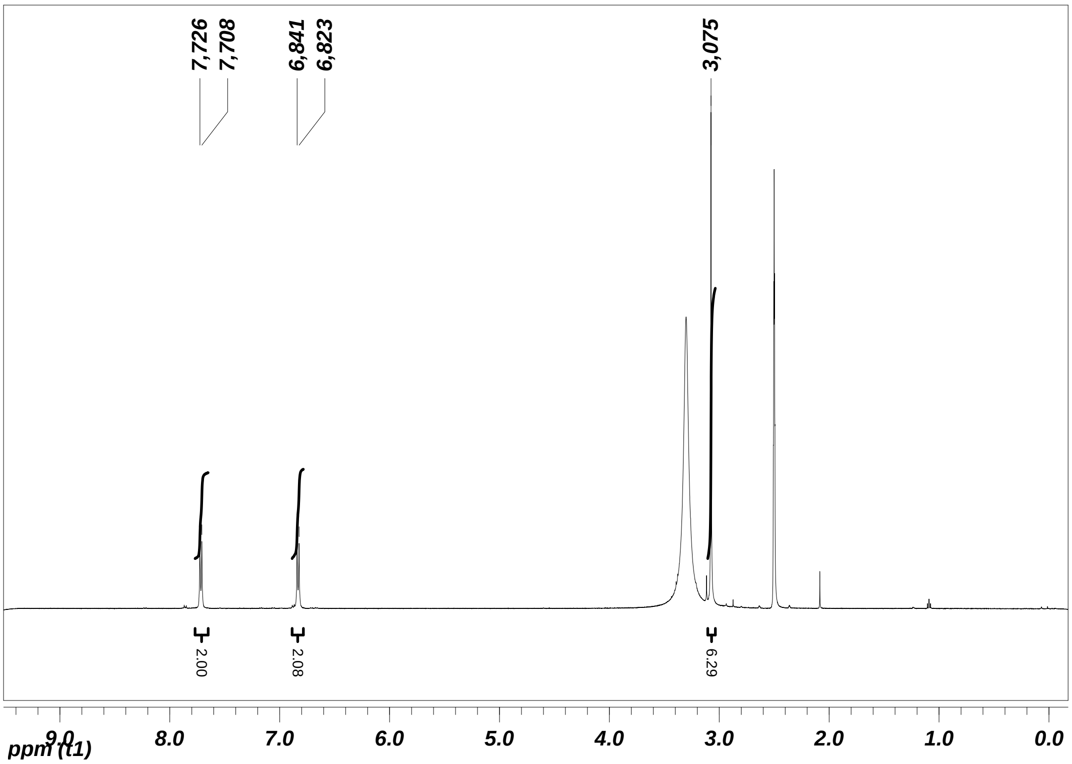


Fig. S3 ^{1}H NMR (500 MHz, DMSO-d_6) of compound **5**.

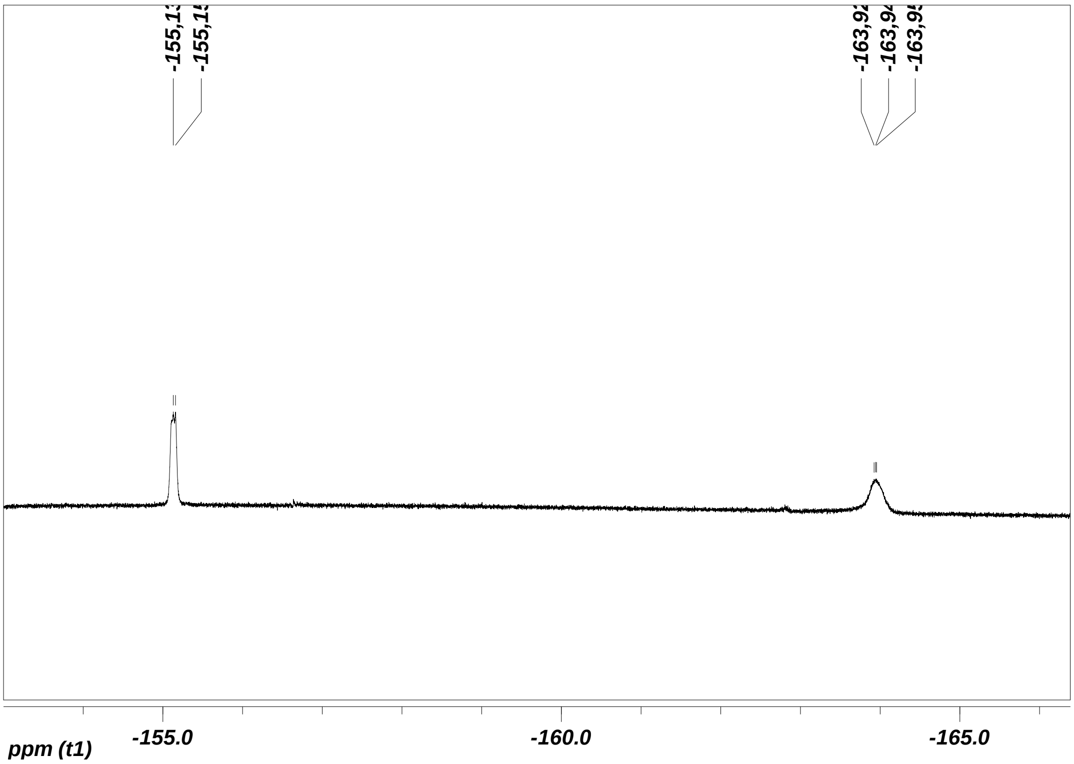


Fig. S4 ^{19}F NMR (475 MHz, DMSO-d_6) of compound **5**.

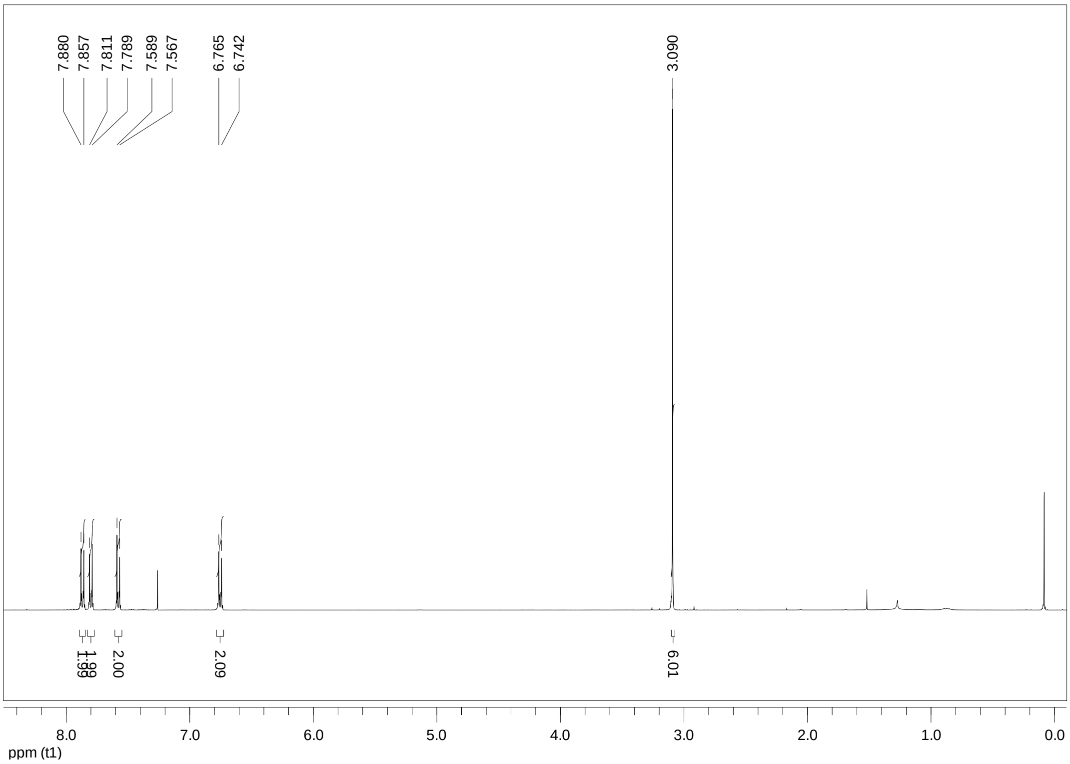


Fig. S5 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **6**.

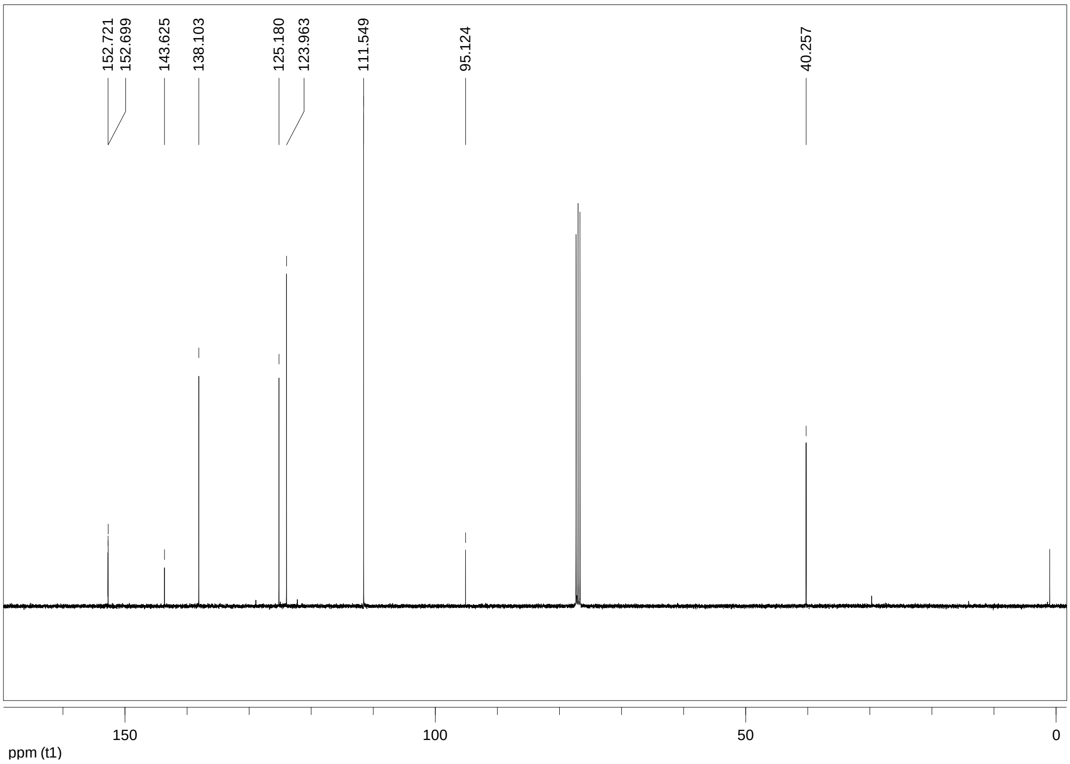


Fig. S6 ^{13}C NMR (400 MHz, $CDCl_3$) of compound **6**.

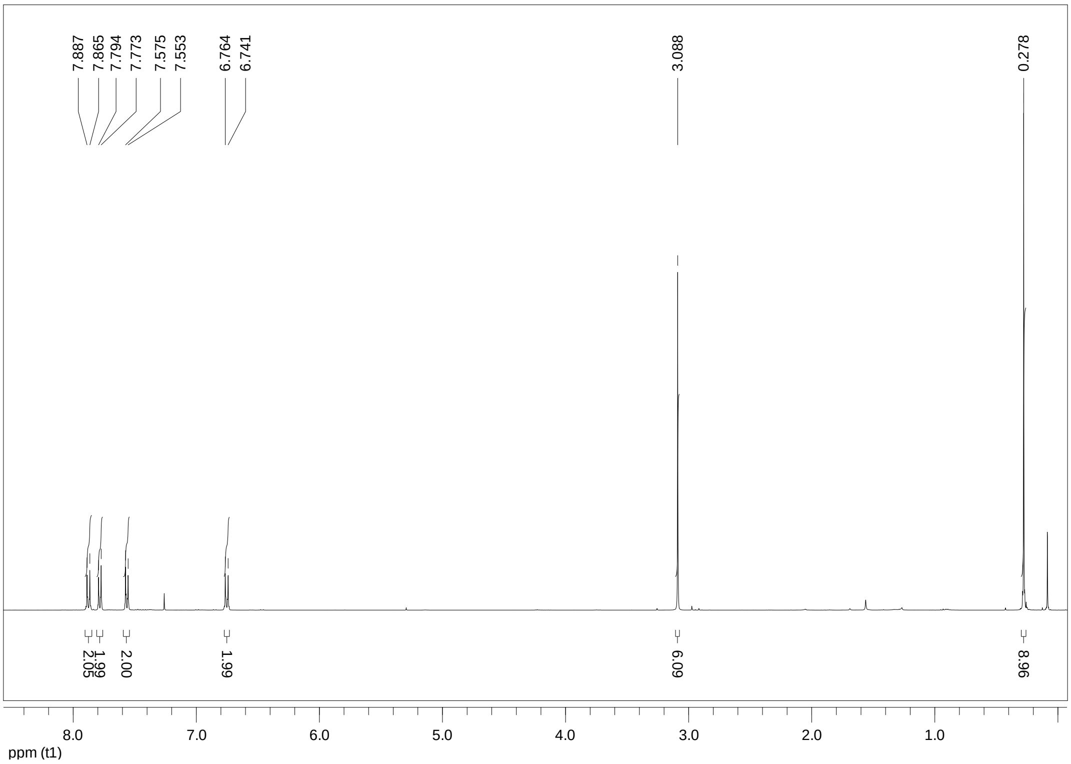


Fig. S7 ^{1}H NMR (400 MHz, CDCl$_3$) of compound **9a**.

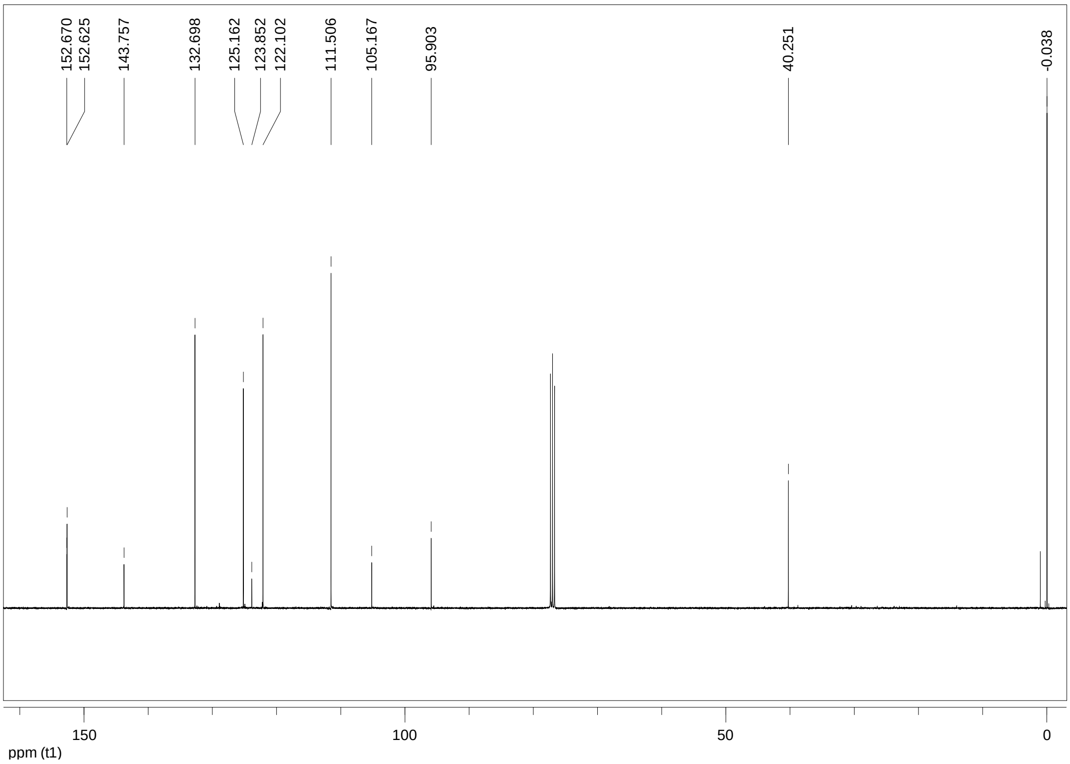


Fig. S8 ^{13}C NMR (400 MHz, CDCl$_3$) of compound **9a**.

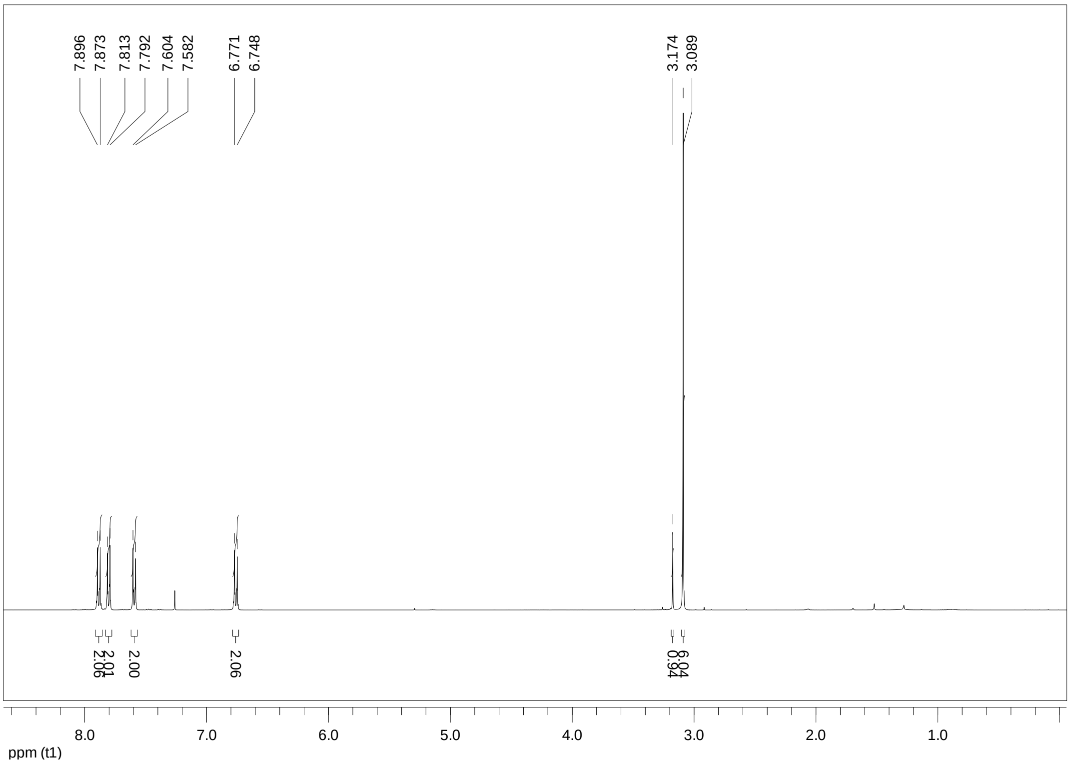


Fig. S9 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**.

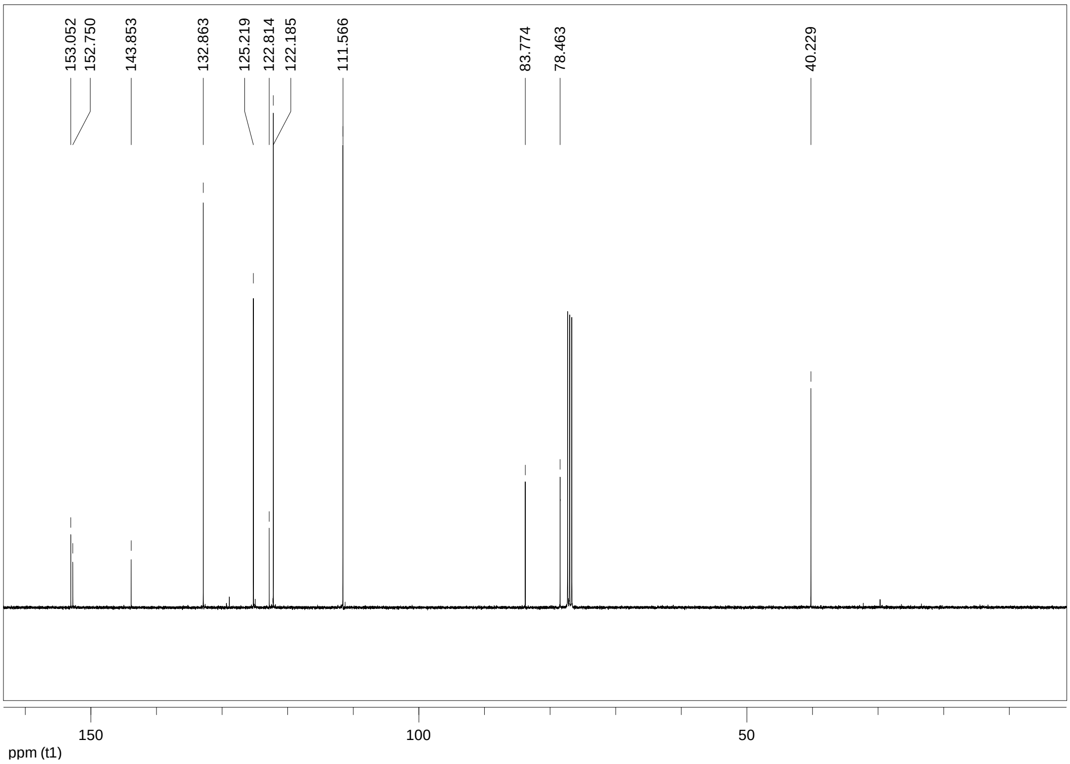


Fig. S10 ^{13}C NMR (400 MHz, $CDCl_3$) of compound **9**.

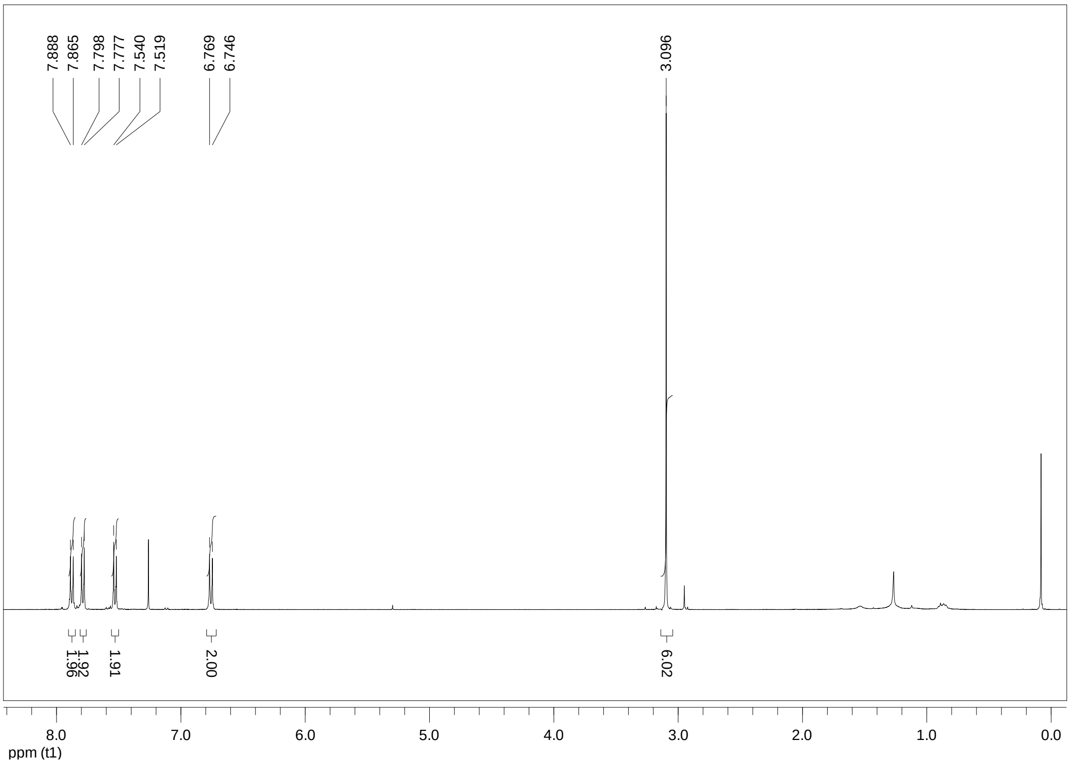


Fig. S11 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **8**.

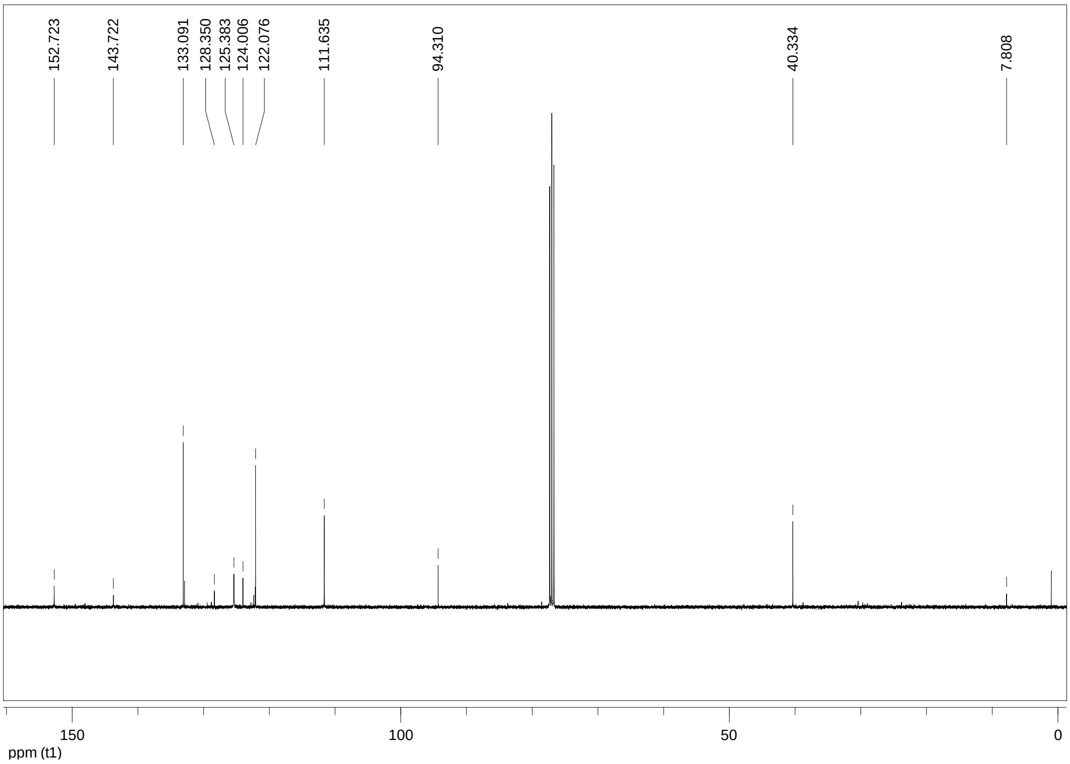


Fig. S12 ^{13}C NMR (400 MHz, $CDCl_3$) of compound **8**.

3. Computational details

Molecular structures of dyes **1-9** were optimized in DMF within the DFT approach, using the PBE0 functional,[S6,S7] which has been judged well suited for describing the electronic and optical features of a series of organic dyes,[S8] and the 6-311++G(d,p) basis set for all atoms. The basis set for iodine[S9] was downloaded from the Basis Set Exchange site.[S10,S11] Solvation effects were included by means of the Polarizable Continuum Model (PCM).[S12] To determine absorption wavelengths, standard vertical Time Dependent[S13-S15] PBE0/6-311++G(d,p) calculations were carried out. The relevant data are collected in Table S1

Molecular dimers of compounds **1-9** with 4-methylpyridine were optimized at the PBE0/6-311++G** level of theory, *in vacuo*. Interaction energies (ΔE_{BSSE}) were computed by optimization on the BSSE-free potential energy surface, as the difference between the energy of the dimer and the sum of the energies of the single monomers. BSSE correction was made by the standard counterpoise method.[S16] All calculations were performed with the Gaussian suite of programs.[S17]

Table S1. Experimental wavelengths (λ_{exp}) and TD-PBE0/6-311++G(d,p) computed data[a] for the dominant low-energy absorption band of compounds **1-9** in DMF. In all cases the absorption bands correspond to charge-transfer transitions from the Highest Occupied (HOMO) to the Lowest Unoccupied Molecular Orbitals (LUMO).

Compound	λ_{exp}	λ	f	μ_{eg}	μ_e	$\Delta\mu$
1	451	469	1.37	11.67	17.86	7.19
2	462	482	1.53	12.52	17.72	7.25
3	462	486	1.60	12.85	17.31	7.09
4	448	472	1.37	11.74	16.54	7.60
5	455	467	1.20	10.91	12.94	5.31
6	435	466	1.48	12.13	16.53	7.25
7	412	455	1.35	11.42	11.62	5.97
8	446	487	1.75	13.45	16.03	7.67
9	441	480	1.56	12.63	16.70	8.40

[a] excitation wavelengths (λ, nm), oscillator strengths (f), transition dipole moments (μ_{eg}, D), excited state dipole moments (μ_e, D) and difference between excited and ground state dipole moments ($\Delta\mu = \mu_e - \mu$, D).

4. Co-crystallization experiments

Preparation of 10·(5)$_2$ co-crystals

Compound **5** and 1,2-di(4-pyridyl)ethylene (**10**) were separately dissolved in methanol (minimum amount) at r.t., in 2:1 molar ratio. The two solutions were then mixed in a clear borosilicate glass vial, which was left open in a closed cylindrical wide-mouth bottle containing diethyl ether, until good-quality single crystals of trimer **10**·(**5**)$_2$ were formed.

Decomposed without melting (T > 188 °C). **FTIR** (cm^{-1}): 1643, 1597, 1558, 1494, 1444, 1407, 1359, 1299, 1229, 1116, 1013, 963, 948, 888, 819, 789, 733, 663.

Preparation of 10·(8)$_2$ co-crystals

Compound **8** and 1,2-di(4-pyridyl)ethylene (**10**) were separately dissolved in tetrahydrofuran (minimum amount) at r.t., in 2:1 molar ratio. The two solutions were then mixed in a clear borosilicate glass vial, which was left open in a closed cylindrical wide-mouth bottle containing paraffin oil until crystals of trimer **10**·(**8**)$_2$ were obtained.

Decomposed without melting (T > 190 °C). **FTIR** (cm^{-1}): 2917, 2849, 1595, 1555, 1512, 1441, 1415, 1355, 1310, 1227, 1155, 1137, 1097, 1059, 999, 974, 955, 941, 852, 821, 551, 540, 450.

5. Single crystal X-ray diffraction analysis

The single-crystal X-ray structures were determined using a Bruker Kappa Apex II CCD diffractometer with Mo *Kα* radiation (λ = 0.71073 Å) and a Bruker Kryoflex low-temperature device. Crystals were mounted in inert oil on glass fibers. Data collection and reduction were performed by SMART[S18] and SAINT[S18] and absorption correction, based on multi-scan procedure, by SADABS.[S18] The structures were solved by SIR92[S19] and refined on all independent reflections by full-matrix least-squares based on F_o^2 by using SHELX-97.[S20]

Crystallographic data are reported in Table S2

CIF containing crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif .

Table S2 Crystallographic data for **10**·(**5**)$_2$ and **10**·(**8**)$_2$ complexes.

	10·(**5**)$_2$	**10**·(**8**)$_2$
Chemical Formula	$C_{40}H_{32}F_8N_8O_2$	$C_{44}H_{38}I_2N_8$
Formula weight	808.74	932.62
Temperature K	103(2)	103(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/m*
a (Å)	14.7987(6)	17.6158(15)
b (Å)	12.0088(6)	7.4356(8)
c (Å)	20.0244(11)	14.8281(15)
α(°)	90.00	90.00
β (°)	90.598(3)	98.184(3)
γ(°)	90.00	90.00
Volume (Å^3)	3558.4(3)	1922.5(3)
Z	4	2
Density (gcm^{-3})	1.510	1.611
μ (mm^{-1})	0.125	1.680
F (000)	1664	928
ABS T_{min}, T_{max}	-	0.6853, 0.7573
$\theta_{min,\ max}$ (°)	2.03, 26.41	2.34, 33.17
No. of reflections.	33495	43168
No. unique reflections.	3647	3916
No of parameter	307	300
No of restarints	416	1016
R_{all}, R_{obs}	0.0645, 0.0378	0.0417, 0.0351
wR_2_{all}, wR_2_{obs}	0.0977, 0.0876	0.0753, 0.0721
$\Delta\rho_{max,\ min}$ (eÅ^{-3})	-0.204, 0.301	-0.940, 3.143
G.o.F	1.015	1.095
CCDC	1025655	1025656

Refine special details for 10·(**5**)$_2$ **co-crystal**. Only the phenolic H atom was refined, all the others were in calculated. The diazo derivative is disordered by a rotation of 180° around the O1···N3 axis. All the atoms of 1-tetrafluorophenyl-2-phenyldiazo group were split. The spatial separation between all the atoms in the tetrafluorophenyl moiety is less than 0.35 Å. To avoid very large parameters correlations all tetrafluorophenyl atoms were refined isotropically.

Refine special details for 10·(**8**)$_2$ **co-crystal**. Both molecule **8** and **10** were very disordered. We modeled the extended rotational disorder of both the molecules with two models (designed as A and

B, see refine instruction details section in the cif file). The population ratio for the iodoethynyl molecule conformations was 0.5/0.5, while for the dipyridylethylene molecule was refined to 0.74/0.26. In the azo-dye **8** only the iodoethynyl moiety, the nitrogen N3, the carbon C12 and methyl group were considered ordered and fixed on the mirror at y=0. The refinement was carried on with a large number of restraints using SADI command for chemically similar atoms and FLAT command for the three aromatic groups. Moreover, we constrained the chemically equivalent atoms of the two independent molecular models to have exactly the same ADPs. A residue of about 3 e/Å^{-3} suggests that the iodine atom is disordered, but when the atom was split the distance I1···I1$_{(x,-y,z)}$ was about 0.27 Å, largely below the data resolution. Based on this we preferred to keep the 'ordered model' for the iodine atom.

Table S2 O···N and I···N distances in **10**·(**5**)$_2$, **10**·(**7**)$_2$,[S2] **10**·(**8**)$_2$ and **C$_6$Cl$_5$OH···4-Me-Py**[S21] complexes.

	10·(**5**)$_2$	**10**·(**7**)$_2$[S2]	**C$_6$Cl$_5$OH···4-Me-Py**[S21]	**10**·(**8**)$_2$
Contact	**O···N**	**I···N**	**O···N**	**I···N**
Distance	2.557(2)	2.703	2.515	2.754(3)

6. Optical and photochemical studies

UV-Vis spectra were collected from both thin films and 10^{-5} M DMF solution with an Ocean Optics USB2000+ fiber-optic spectrometer and a DH-2000-BAL light source, both in dark and under irradiation (488 nm, 50 mW/cm2). Thermal *cis-trans* isomerization was studied by exciting the chromophores with a circularly polarized pump beam (488 nm, 50 mW cm^{-2}) and monitoring the transmittance changes after blocking the pump. The probe was a fiber-coupled xenon lamp equipped with proper bandpass filters. The signal was detected with a photodiode and a lock-in amplifier.

SRG inscription was performed using a spatially filtered and collimated Ar^+ laser beam with circular polarization at wavelength of 488 nm with an irradiation intensity of 150 mW cm^{-2}. Lloyd mirror interferometer, with an incidence angle of 15° (spatial period of 1 μm) was used to create the light-interference pattern. The time evolution of the gratings was monitored by collecting the transmitted first-order diffraction of a normally incident 633 nm He-Ne laser beam in transmission mode using an oscilloscope. The diffraction efficiency of the gratings was defined as $\eta = I_1 / I_0$, where I_1 and I_0 are the intensities of the first-order diffracted beam and the transmitted beam prior to irradiation, respectively.

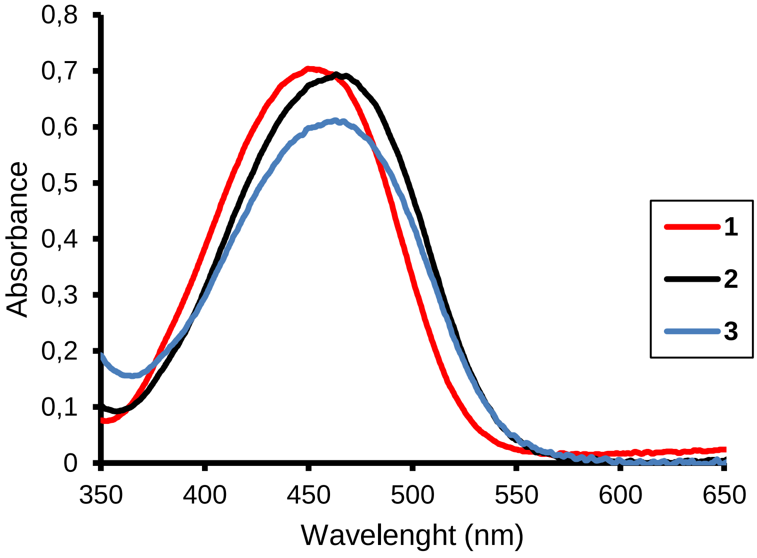


Fig. S13 UV spectra of the compounds **1**, **2** and **3** in diluted (10^{-5} M) DMF solution.

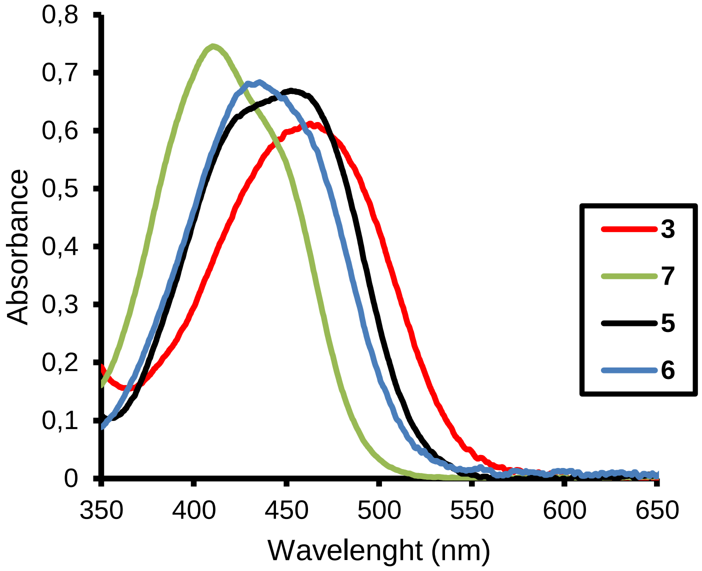


Fig. S14 UV spectra of the compounds **3**, **5**, **6** and **7** in diluted (10^{-5} M) DMF solution.

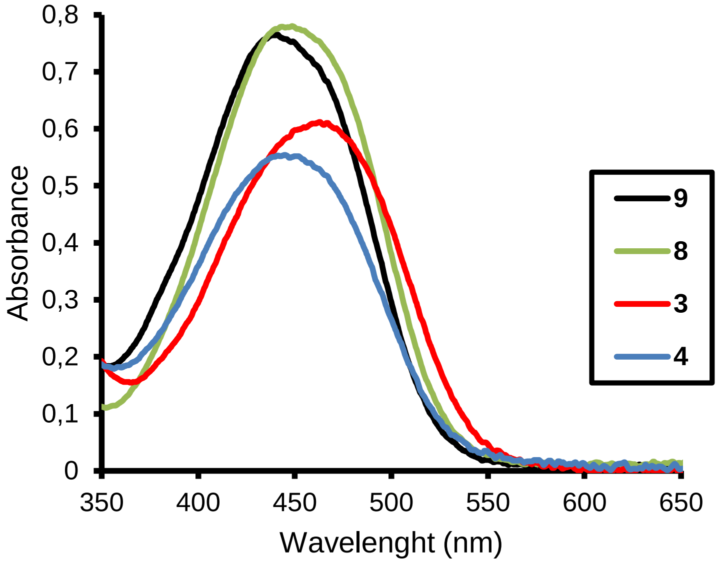


Fig. S15 UV spectra of the compounds **3**, **4**, **8** and **9** in diluted (10^{-5} M) DMF solution.

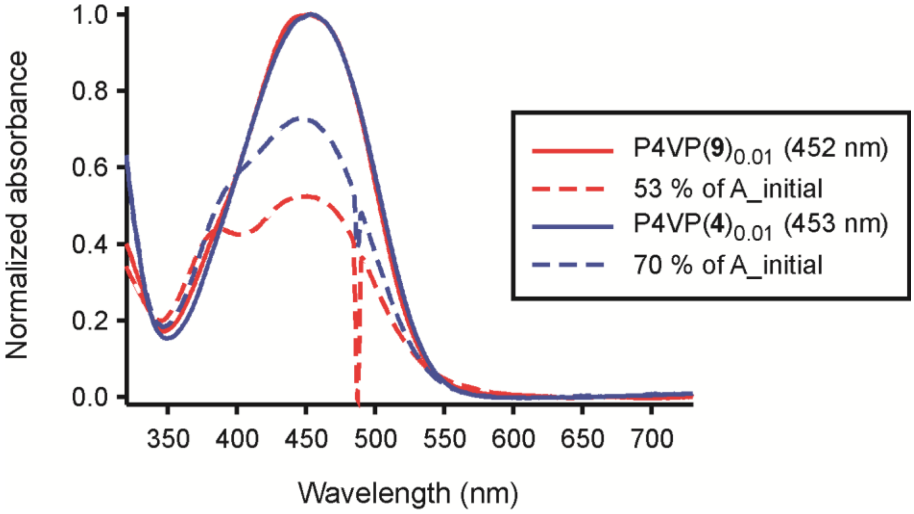


Fig. S16 UV spectra before irradiation (solid lines) and after irradiation (dotted lines) for the thin films of P4VP complexes with azodyes **9** and **4**. 1 mol% loading of the dye was used.

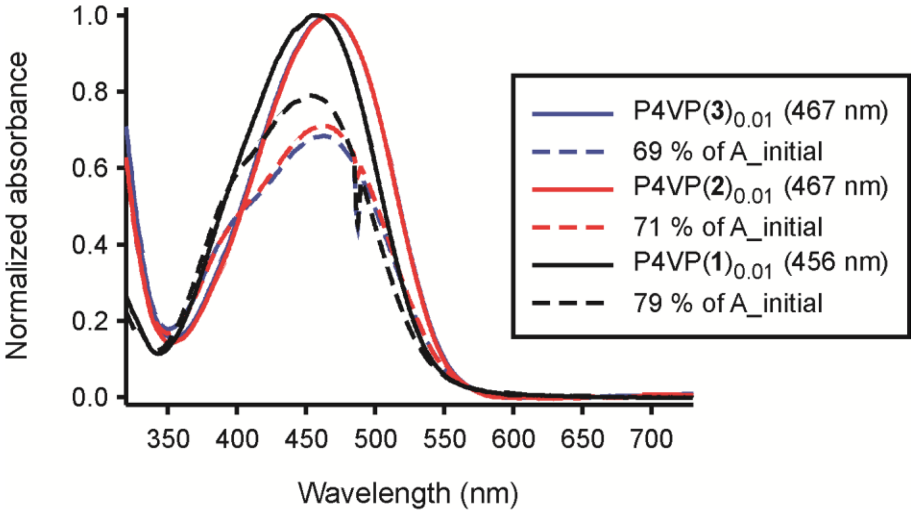


Fig. S17 UV spectra before irradiation (solid lines) and after irradiation (dotted lines) for the thin films of P4VP complexes with azodyes **3**, **2** and **1**. 1 mol% loading of the dye was used.

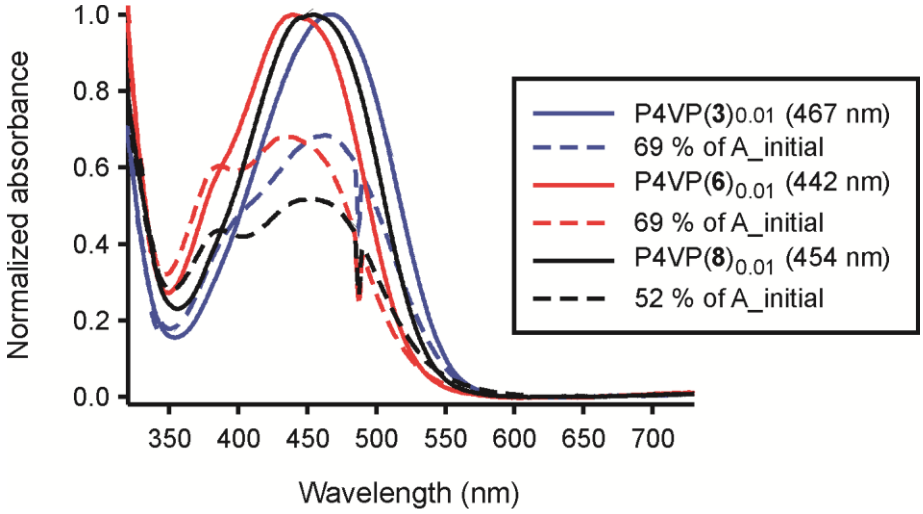


Fig. S18 UV spectra before irradiation (solid lines) and after irradiation (dotted lines) for the thin films of P4VP complexes with azodyes **3**, **6** and **8**. 1 mol% loading of the dye was used.

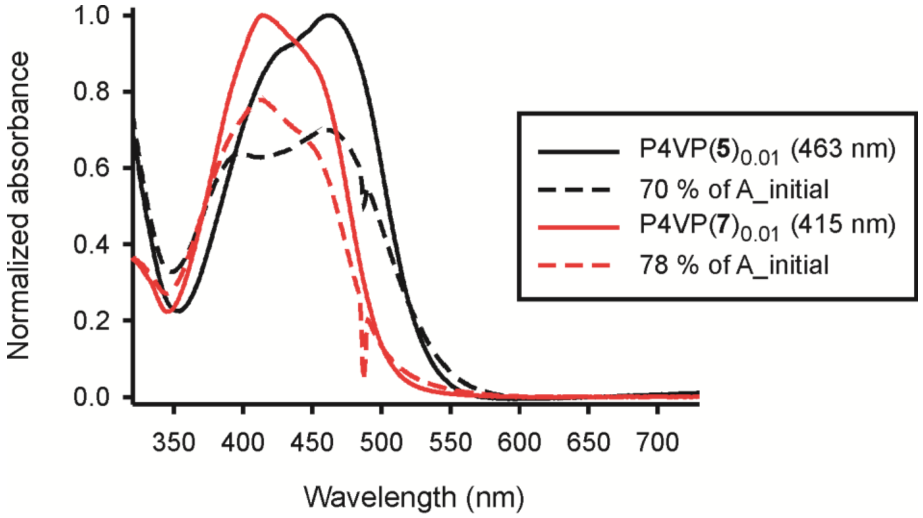


Fig. S16 UV spectra before irradiation (solid lines) and after irradiation (dotted lines) for the thin films of P4VP complexes with azodyes **6** and **7**. 1 mol% loading of the dye was used.

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