Electronic Supplementary Information
Indanthrone dye revisited after sixty years

Kamil Kotwica[a], Piotr Bujak[a*], Damian Wamil[a], Mariusz Materna[a], Lukasz Skorka[a], Piotr A. Gunka[a], Robert Nowakowski[b], Barbara Golec[b], Beata Luszczynska[c] , Malgorzata Zagorska[a] and Adam Pron[a]

[a]Faculty of Chemistry, Warsaw University of Technology Noakowskiego 3, 00-664 Warsaw, Poland
[b]Institute of Physical Chemistry, Polish Academy of Science, Kasprzaka 44/52, 01-224 Warsaw, Poland
[c]Department of Molecular Physics, Technical University of Lodz, Zeromskiego 116, 90-924 Lodz, Poland

Corresponding Author
*E-mail: piotrbujakchem@poczta.onet.pl.

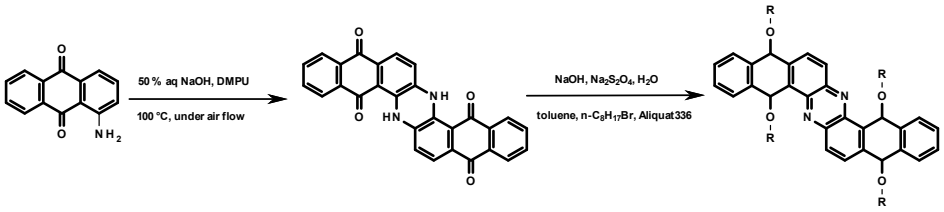
Experimental

Characterization techniques

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer and referenced with respect to TMS and solvents. Solid state FT-IR spectra were recorded on a Nicolet 6700 FTIR-ATR spectrometer (Thermo Scientific). Mass spectra (FD^{+}) and (EI^{+}) were registered on a GCT Premier (Waters) spectrometer and on an AutoSpec Premier (Waters) spectrometer, respectively. The elemental analyses were carried out on a Vario EL III (Elementar) CHN analyzer. UV-vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. Steady-state fluorescence was recorded using Edinburgh FS 900 CDT fluorometer (Edinburgh Analytical Instruments). Emission quantum yield were measured using quinine sulfate in 0.05 mol dm^{-3} H_2SO_4 (φ_{fl} = 0.51) as a standard.[1] Fluorescence life times were recorded using a home-built time-resolved single photon counting (SPC) technique. The excitation was provided by IBH Nanoled emitting at 297 nm with pulse width <750 ps. The SPC setup consisted also of Spectral Products Digikrom CM 110 monochromator, Becker & Hickl PMC 100-4 photomultiplier and PicoQuant TimeHarp 100 PC card. The decay curves were analyzed using PicoQuant Fluofit version 3.3.

Chemicals

1-aminoanthraquinone, 1,3-dimethlyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), NaOH, sodium dithionite, 6,15-dihydrodinaptho[2,3-a:2',3'-h]phenazine-5,9,14,18-tetraone (indanthrone), 1-bromooctane were purchased from Sigma-Aldrich Corporation and used as received.



Scheme S1. Synthetic route to **P-C8**

Synthesis of 6,15-dihydrodinaptho[2,3-a:2',3'-h]phenazine-5,9,14,18-tetraone, indanthrone (see Scheme S1)

A 250-ml glass reactor, equipped with a mechanical stirrer, a dropping funnel, a thermometer and an aeration system, was charged with 5.0 g (0.02 mol) of 1-aminoanthraquinone and 15.4 g (0.12 mol) of 1,3-dimethlyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU). The charged reactor was then heated under air flow to 100 °C. At this temperature aqueous solution of NaOH (18 M, 6.6 mL) was added and the reaction mixture was stirred for 24 hours. It was then allowed to cool down to room temperature, yielding a precipitate which was isolated by filtration. The precipitate was then transferred to a separate flask and mixed with aqueous solution of NaOH (1.7 M, 165 mL). The flask was heated to 60 °C and then 2.8 g (0.02) of sodium dithionite were added. The reaction mixture was kept at this temperature for 30 minutes, it was then allowed to cool down to 50 °C and subsequently filtered using a Buchner funnel. The separated precipitate was consecutively washed with methanol and water and finally dried in air for 72 hours to give 3.9 g of indanthrone (90% yield). Anal. Calcd for $C_{28}H_{14}N_2O_4$ C, 76.01; H, 3.16; N, 6.33, Found: C, 75.28; H, 2.85; N 6.30, (For the indanthrone purchased from Sigma-Aldrich, Found: C, 75.32; H, 3.60; N, 6.54.)

5,9,14,18-tetraoktyoxydinaptho[2,3-a:2',3'-h]phenazine, P-C8 (see Scheme S1)

A 250-mL three-necked flask equipped with a magnetic stirrer, a condenser and a dropping funnel was charged with an aqueous solution of NaOH (1.6 M, 75 mL) and, subsequently, the

whole system was purged with argon (15 min). The solution was then heated to 60 °C, whereupon 0.394 g (0.0022 mol) of sodium dithionite and 1.0 g (0.0022 mol) of **6,15-dihydrodinaptho[2,3-a:2',3'-h]phenazine-5,9,14,18-tetraone** (indanthrone) were added. The resulting mixture was stirred for 1 hour, then 50 mL toluene and 4.1 mL of Aliquat 336 were added. The mixture was then heated to 110 °C and subsequently 2.3 mL of 1-bromoctane (0.009 mol) were added. It was kept at this temperature for 24 hours and then allowed to cool down to room temperature and subsequently neutralized by drop-wise addition of 5% aqueous solution of hydrochloric acid. The product was extracted with dichloromethane, the combined organic phases were dried over anhydrous magnesium sulfate and concentrated to yield a dark blue solid. The crude product was purified by column chromatography (eluent: CH_2Cl_2) and then recrystallized from THF to give a yellow solid (588 mg, 30%) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91-0.95 ppm (m, 4×CH_3, 12H), 1.34-1.55 (m, ~~4×4×4×CH_2, 16H~~ 4×4×CH_2, 32H), 1.69-1.78 (m, 4×CH_2, 8H), 2.09-2.15 (m, 2×CH_2, 4H), 2.30-2.35 (m, 2×CH_2, 4H), 4.24 (t, *J* = 6.6 Hz, 2×OCH_2, 4H), 4.30 (t, *J* = 6.7 Hz, 2×OCH_2, 4H), 7.68-7.73 (m, 4×CH, 4H), 8.04 (d, J = 9.5 Hz, 2×CH, 2H), 8.37-8.41 (m, 2×CH, 2H), 8.50 (d, J = 9.5 Hz, 2×CH, 2H), 8.66-8.70 (m, 2×CH, 2H), ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.2 ppm (2×CH_3), 13.2 (2×CH_3), 21.8 (2×CH_2), 21.8 (2×CH_2), 25.4 (2×CH_2), 25.6 (2×CH_2), 28.5 (2×CH_2), 28.6 (2×CH_2), 28.8 (2×CH_2), 28.9 (2×CH_2), 29.7 (2×CH_2), 29.8 (2×CH_2), 31.0 (2×CH_2), 31.1 (2×CH_2), 74.1 (2×OCH_2), 76.1 (2×OCH_2), 119.9 (2×CH), 122.4 (2×CH), 124.1 (2×CH), 124.6 (2×CH), 126.3 (2×CH), 126.8 (2×CH), 126.9 (2×CH), 127.3 (2×CH), 127.8 (2×CH), 129.0 (2×CH), 141.9 (2×CH), 142.4 (2×CH), 148.3 (2×CH), 151.8 (2×CH), IR (film): 2927, 2856, 1468, 1408, 1374, 1355, 1329, 1317, 1276, 1198, 1126, 1083, 1023, 1009, 949, 902, 818, 758, 724, 687, 626, 595 cm^{-1}. MS (m/z): Calculated for $C_{60}H_{81}N_2O_4$ $[M+H]^+$ 893.61963 found 893.6 (MS, FD^+) and $C_{60}H_{80}N_2O_4$ $[M^{+\bullet}]$ 892.61109 found 892.7 (EI^+). Anal. Calcd for $C_{60}H_{80}N_2O_4$ (%): C, 80.77; H, 8.96; N, 3.13. Found (%): C, 80.51; H, 9.01; N, 3.05.

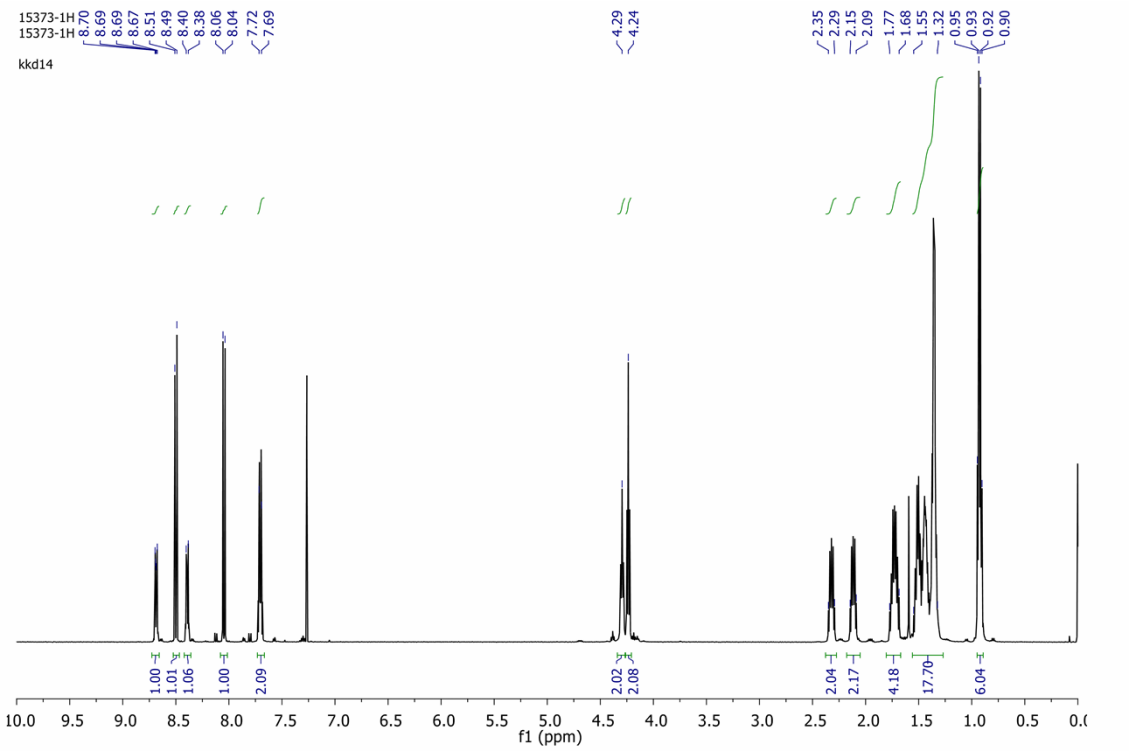


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **P-C8**.

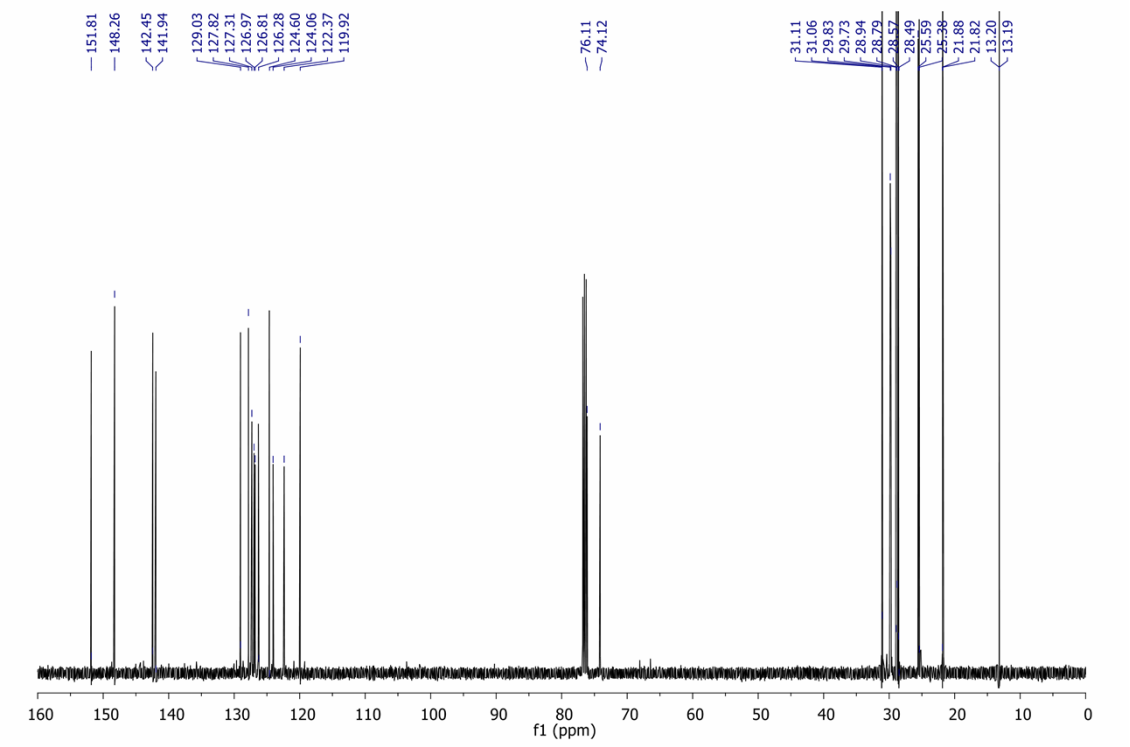


Figure S2. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **P-C8**.

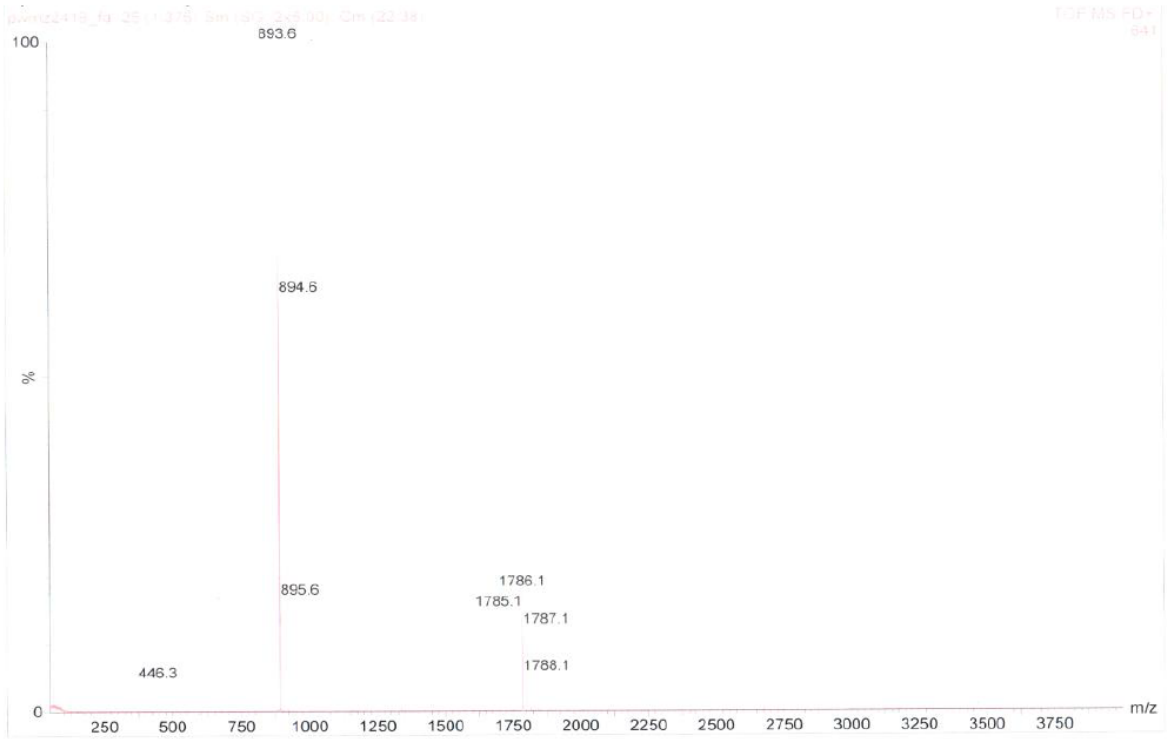


Figure S3. Mass spectrum (FD^+) of **P-C8.**

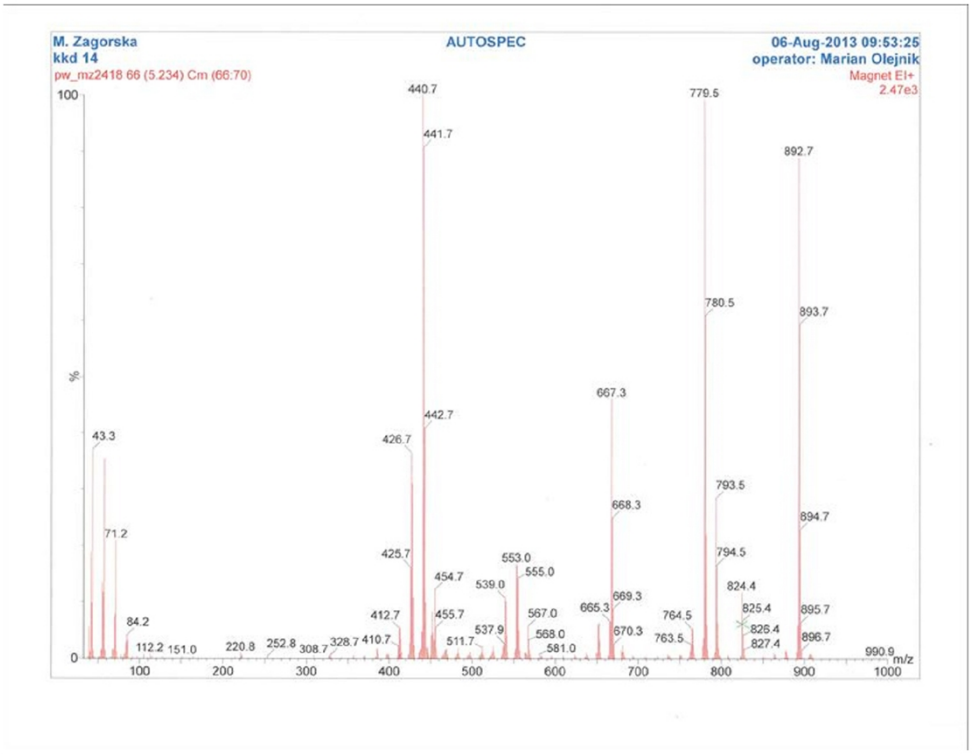


Figure S4. Mass spectrum (EI^+) of **P-C8.**

Single-Crystal X-Ray Diffraction Analysis

Single crystals of **P-C8** suitable for X-ray studies were grown from THF solution. Diffraction data were obtained on an Agilent κ-CCD Gemini A Ultra diffractometer with graphite monochromated Mo-Kα radiation at 100(2) K. Cell refinement and data collection as well as data reduction and analysis were performed with the CrysAlis^{PRO} software.[3] The structure was solved by direct methods and subsequent Fourier-difference synthesis with SHELXS-97 and refined by full-matrix least-squares against F^2 with SHELXL-97[4] within the OLEX2 program suite.[5] All non-hydrogen atoms were refined anisotropically.

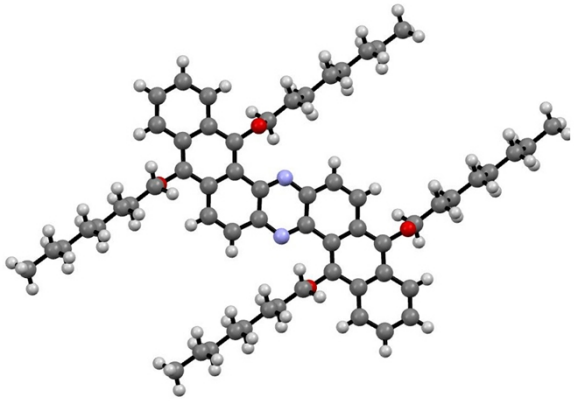


Table S1. Crystallographic data of **P-C8.**

CCDC	**1006274**
Chemical formula	$C_{60}H_{80}N_2O_4$
Formula weight	893.26
Crystal system	triclinic
Space group	
a /Å	9.93781(14)
b /Å	15.1528(2)
c /Å	17.8125(2)
α /°	69.7564(13)
β /°	88.9555(11)
γ /°	87.1772(12)
V /Å^3	2513.57(7)
Z	2
T /K	100
Radiation	MoKα (λ = 0.71073)
ρ_{calc} /mg/mm^3	1.180
μ(MoKα) /mm^{-1}	0.072
F(000)	972.0

Crystal size/mm^3	0.43 × 0.25 × 0.06
2Θ range for data collection	4.104 to 65.694°
Index ranges	$-15 \le h \le 14$, $-22 \le k \le 22$, $-27 \le l \le 26$
Reflections collected	99579
Independent reflections	17538 [R_{int} = 0.0420, R_{sigma} = 0.0320]
Data/restraints/parameters	17538/0/599
Goodness-of-fit on F^2	1.024
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0513, wR_2 = 0.1326
Final *R* indexes [all data]	R_1 = 0.0809, wR_2 = 0.1543
Largest diff. peak/hole / eÅ^{-3}	0.52 /−0.24

STM investigations

Monomolecular layers for STM investigations were deposited by drop-casting from a solution in hexane (~1.5 mg/L) on a freshly cleaved surface of highly oriented pyrolitic graphite (HOPG, SPI Supplies, USA). After evaporation of the solvent in air, the samples were imaged in ambient conditions using an STM system fabricated at the University of Bonn, Germany.[2] All images were recorded with mechanically cut Pt/Ir (80/20 %) tips.

Cyclic voltammetry studies

Electrochemical properties of **P-C8** were investigated using cyclic voltammetry (CV). All cyclic voltammograms were recorded in a dry argon atmosphere on an Autolab potentiostat (Eco Chimie) using a platinum working electrode of the surface area of 3 mm^2, a platinum wire counter electrode and an Ag/0.1 M $AgNO_3/CH_3CN$ reference electrode. The electrolytic medium consisted of the compound studied (c = 5×10^{-4} M) dissolved in a 0.1 M Bu_4NBF_4/dichloromethane electrolyte. The potential of the reference electrode with respect to the ferrocene redox couple was always measured after each experiment. The ionization potential (IP) and electron affinity (EA) were calculated from the oxidation and reduction onsets using equations 1 and 2, where -5.1 V stands for the formal potential (E^0) of the Fc/Fc^+ redox couple expressed on the absolute potential scale (i.e., with respect to the vacuum level).[6]

$$IP(eV) = |e|(E_{ox(onset)} + 5.1) \quad \textbf{(1)} \qquad EA(eV) = -|e|(E_{red(onset)} + 5.1) \quad \textbf{(2)}$$

Table S2. Redox potentials (measured vs Ag/Ag+ and Fc/Fc+ couple) and electrochemically deteremined ionization potential and electron affinity for **P-C8**

$E_{ox(onset)}$ [V] (Ag/Ag+)	$E_{red(onset)}$ [V] (Ag/Ag+)	$E_{ox(onset)}$ [V] (Fc/Fc+)	$E_{red(onset)}$ [V] (Fc/Fc+)	IP [eV]	EA [eV]
0.69	-1.2	0.54	-1.35	5.79	-3.90

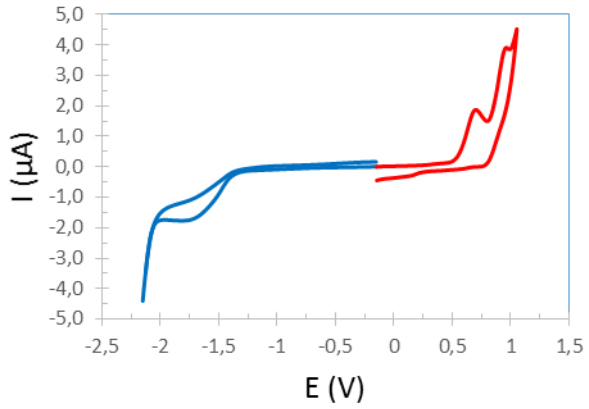


Figure S5 Cyclic voltammogram of **P-C8** , scan rate = 50 mV/s, electrolyte 0.1 M Bu_4NBF_4 in CH_2Cl_2.

DFT calculations

DFT calculations were carried out using Gaussian09 Revision D.01[7] package and employing hybrid B3LYP[8-10] exchange correlation potential combined with 6-31G(d,p) basis set. Ground-state geometries were fully optimized until a stable local minimum was found, which was confirmed by normal-mode analysis (no imaginary frequencies were present). Symmetry constrains were used imposing C_i point group for neutral species. The ground-state geometries were then reoptimized in solution using polarizable continuum model (PCM)[10] at the same level of theory with dichloromethane as solvent. The oscillator strengths and energies of the vertical singlet excitations were calculated employing time-dependant version (TD) of DFT[12-18] and again at the same level of theory (B3LYP/6-31G(d,p)). The TD-DFT results were retrieved from output files using GaussSum 2.2.[19] The nature of the multiconfiturational transitions was analyzed with natural transition orbitals.[20] Molecular orbital plots were generated with the aid of Gabedit 2.4.6.[21] Spin densities were plotted with gOpenmol 3.00.[22,23]

	HOMO A_g	LUMO A_u
Vacuum	-4.99	-1.92
CH_2Cl_2	-5.19	-2.13

Form	Vacuum	DCM
Neutral	-2745.16432192 Hartree	-2745.17493968 Hartree
Radical cation	-2744.94577722 Hartree	-2744.98713888 Hartree
Radical anion	-2745.19920824 Hartree	-2745.25706731 Hartree

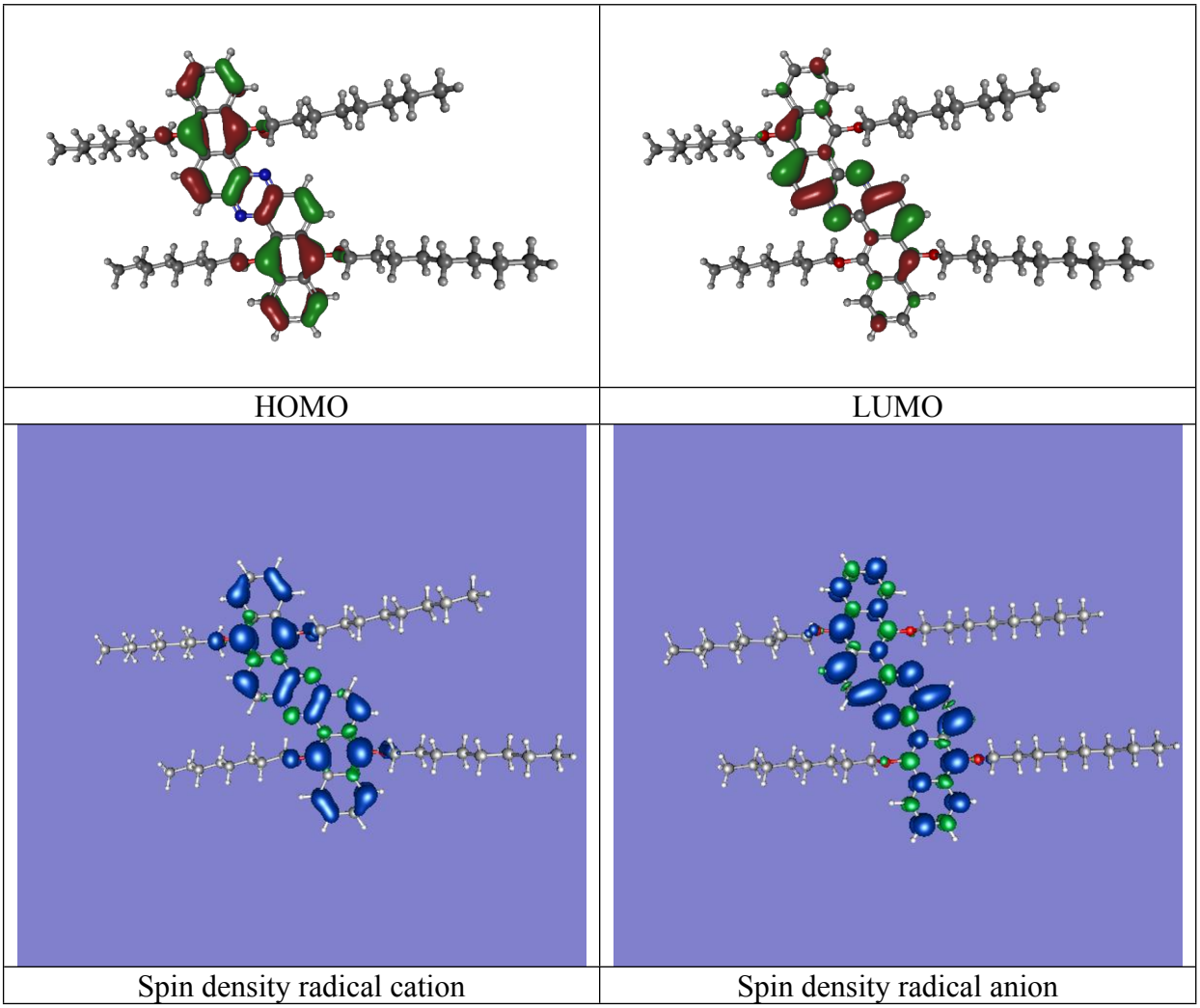
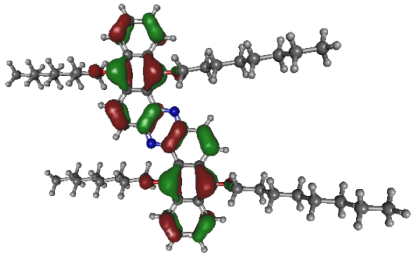
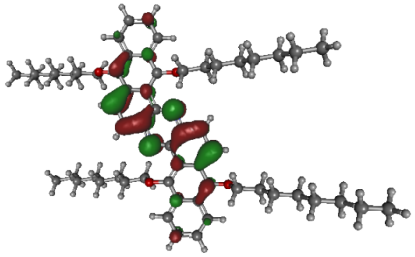
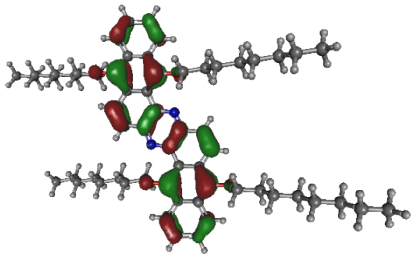
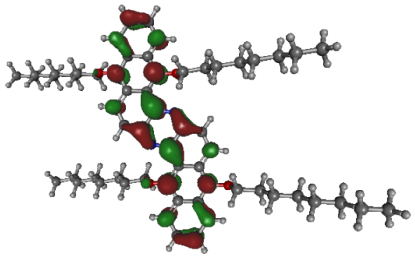
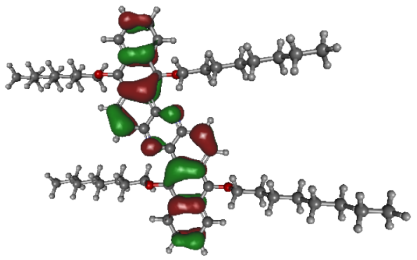
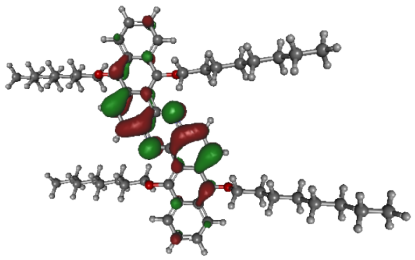
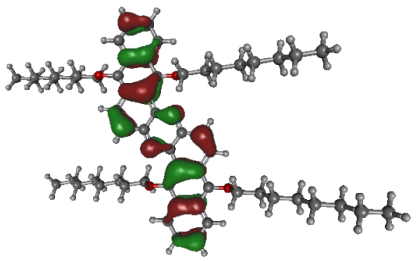
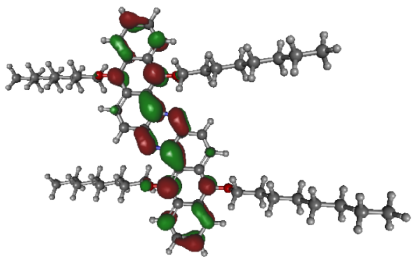
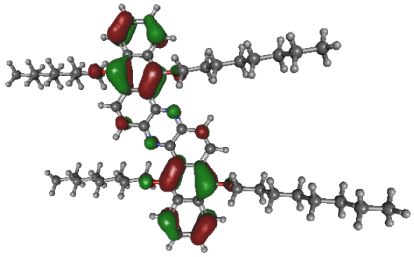
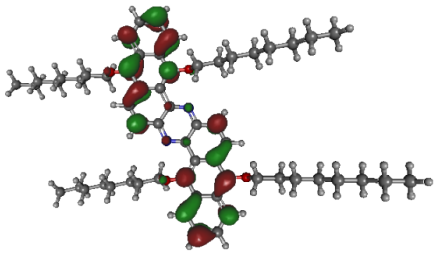
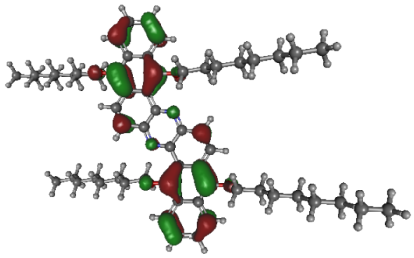
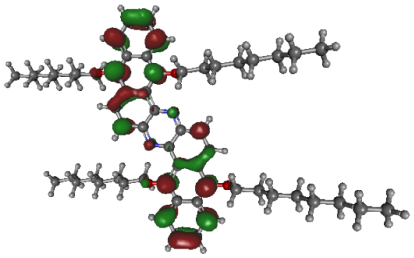
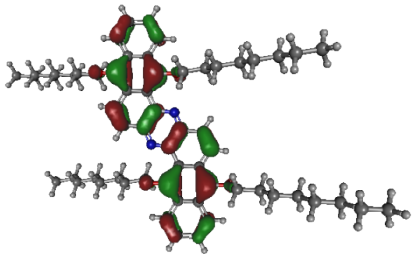
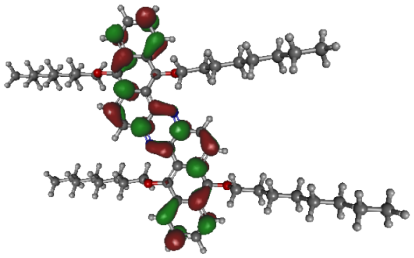


Figure S6. Frontier molecular orbital plots (up, isosurface value = 0.003) and spin densities for radical cation and anion (down isosurface value = 0.001)

Table S3. Natural transition orbitals

No.	Wavelength (nm)	Osc. Strength	Symmetry	Major contribution	λ_{max}
1	476.053358315	0.7432	Singlet-	HOMO->LUMO (94%)	

			AU		
					0.97314
HOTO				LUTO	
2	442.813445621	0.113	Singlet-AU	HOMO->L+1 (94%)	
					0.97533
HOTO				LUTO	
8	336.007308164	0.1236	Singlet-AU	H-2->LUMO (93%)	
					0.94327
HOTO				LUTO	
9	327.625549347	0.9459	Singlet-AU	H-2->L+1 (81%) H-1->L+2 (-10%)	
					0.83214
HOTO				LUTO	

 					0.11547
HOTO-1				LUTO+1	
10	319.923973369	0.5341	Singlet-AU	H-1->L+2 (88%)	
 					0.88566
HOTO				LUTO	
13	293.813300724	0.449	Singlet-AU	H-5->LUMO (10%) H-5->L+1 (11%) HOMO->L+4 (70%)	
 					0.69992
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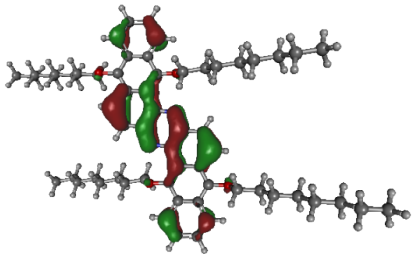
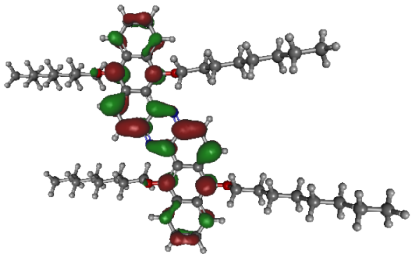
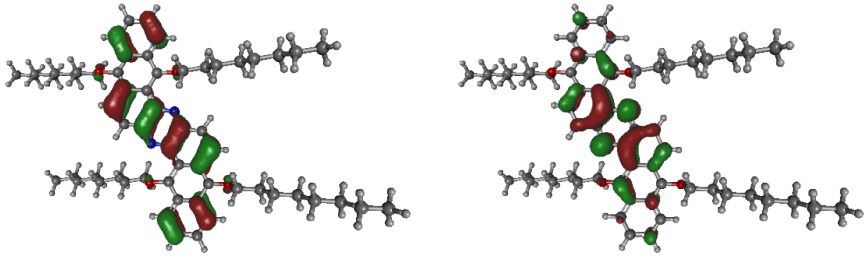
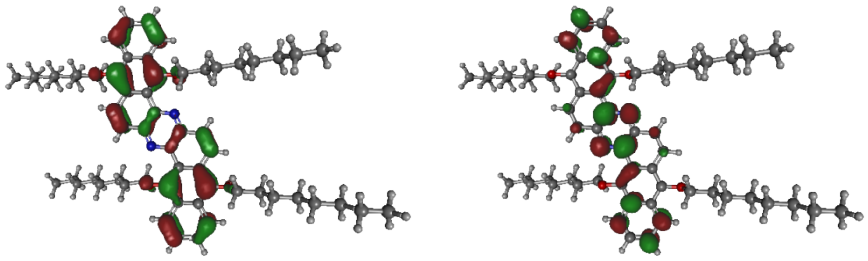
 					0.25707
HOTO-1				LUTO+1	
15	285.45883692	0.1845	Singlet-AU	H-5->LUMO (61%) H-5->L+1 (-24%)	

					0.85217
HOTO				LUTO	
20	271.976783748	0.3137	Singlet-AU	H-5->L+1 (-11%) H-4->L+2 (13%) H-1->L+3 (27%) HOMO->L+5 (32%)	
					0.32167
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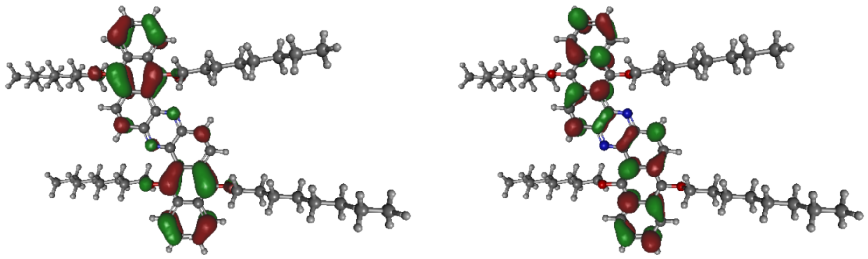					0.27455
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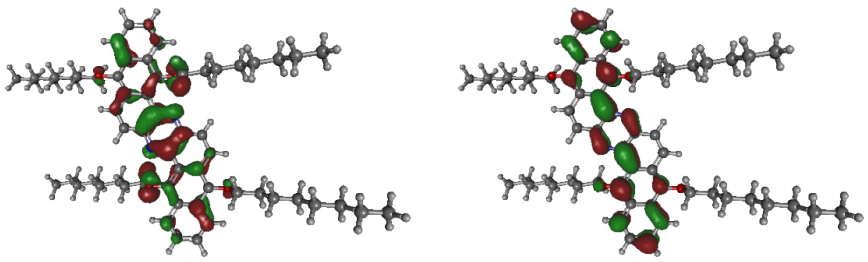
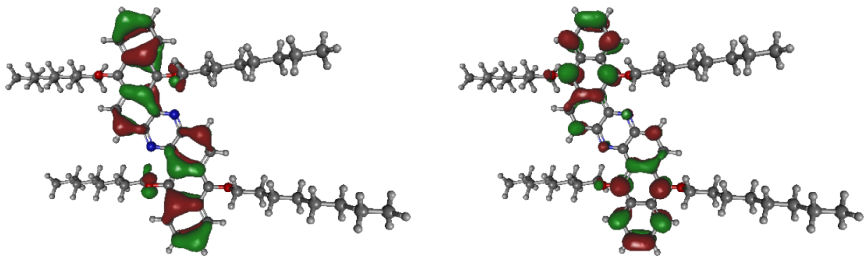
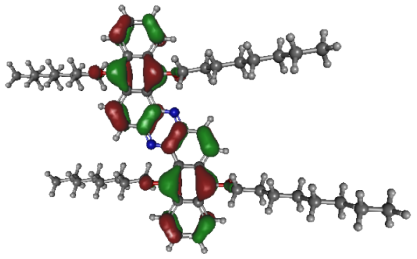
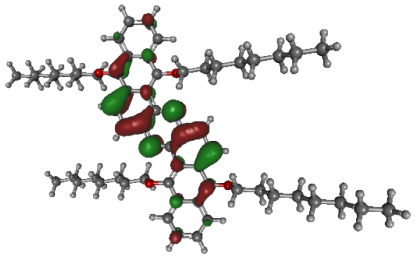
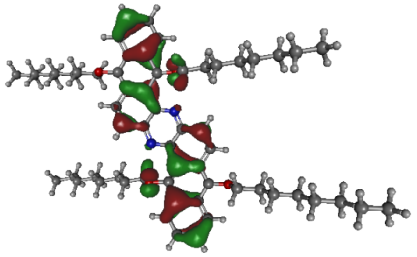
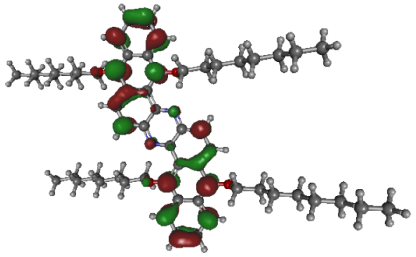
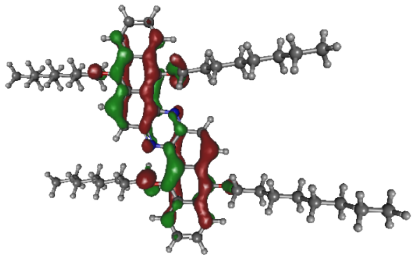
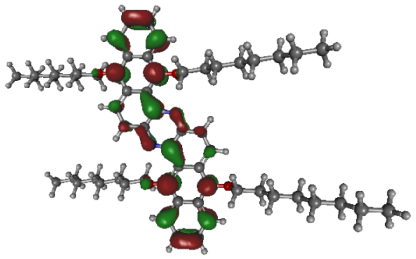
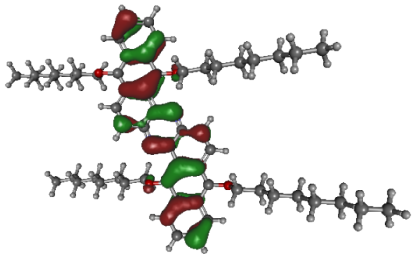
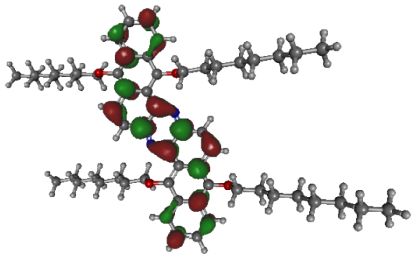
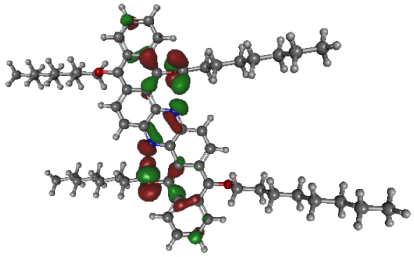
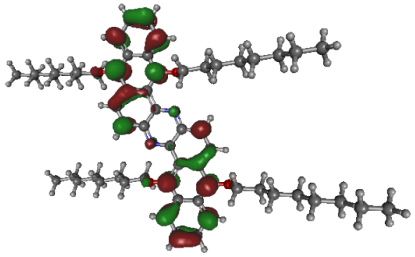
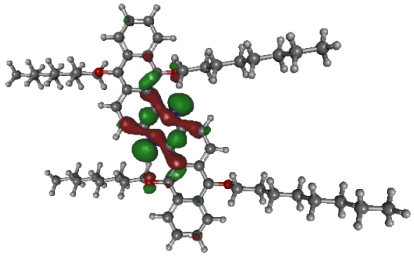
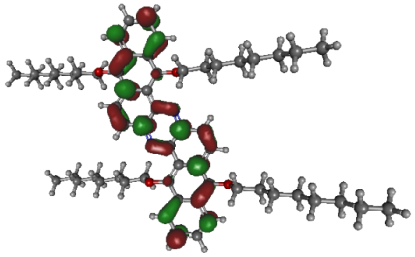
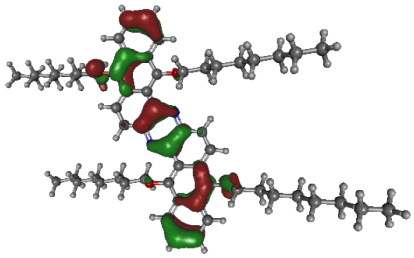
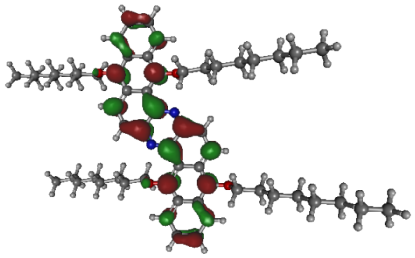
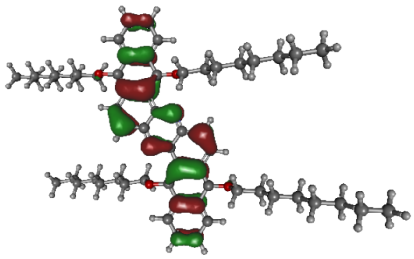
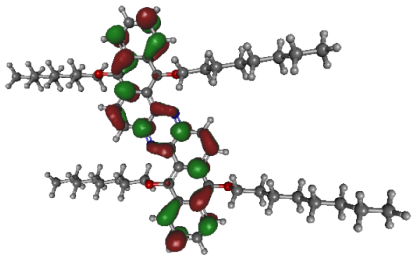
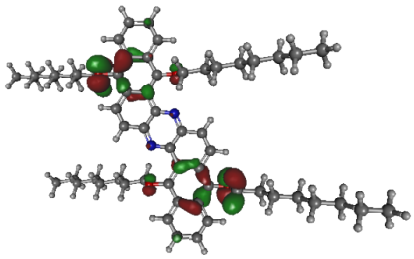
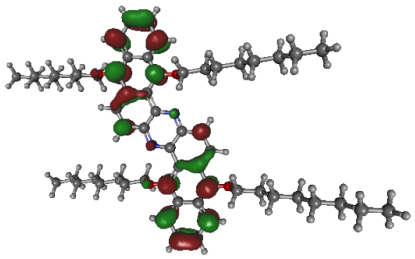
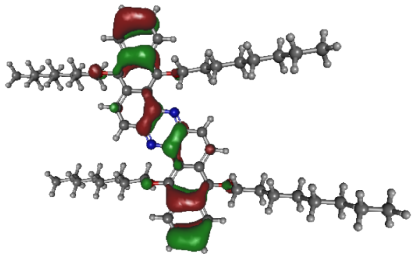
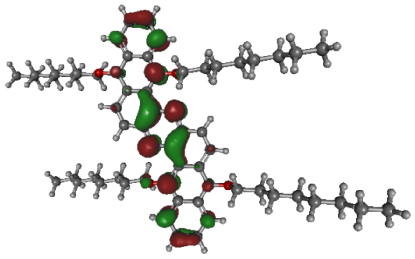
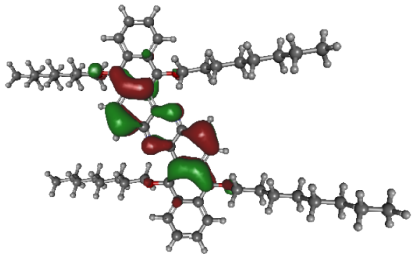
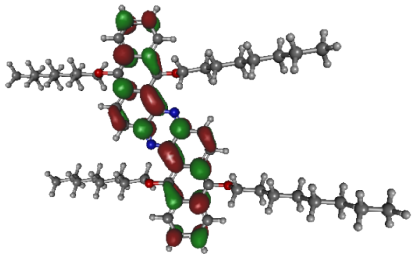
					0.22373
HOTO-2				LUTO+2	
					0.13679

HOTO-3				LUTO+3	
21	268.01413022	0.1035	Singlet-AU	H-8->LUMO (44%) H-8->L+1 (-37%)	
 					0.84113
HOTO				LUTO	
37	240.245192783	0.6606	Singlet-AU	H-11->L+1 (-10%) H-4->L+2 (43%) H-2->L+4 (-14%)	
 					0.51603
HOTO				LUTO	
 					0.19937
HOTO-1				LUTO+1	
 					0.15736
HOTO-2				LUTO+2	
41	234.816925454	0.1187	Singlet-AU	H-6->L+2 (64%) H-3->L+4 (18%)	

					0.67791
HOTO				LUTO	
					0.23351
HOTO-1				LUTO+1	
49	224.002848542	0.1316	Singlet-AU	H-12->L+1 (39%) H-7->L+2 (-11%) H-2->L+4 (-26%)	
					0.48060
HOTO				LUTO	
					0.27521
HOTO-1				LUTO+1	
					0.19886
HOTO-2				LUTO+2	

50	222.291952738	0.3379	Singlet-AU	H-12->L+1 (23%) H-2->L+4 (26%)	
					0.32196
HOTO				LUTO	
					0.29705
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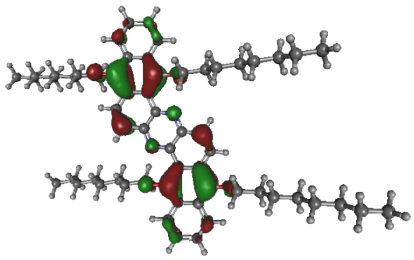
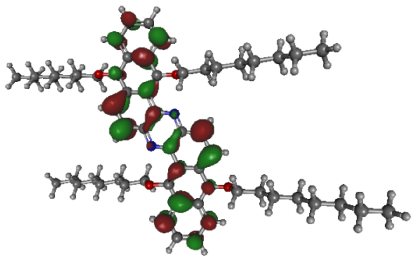
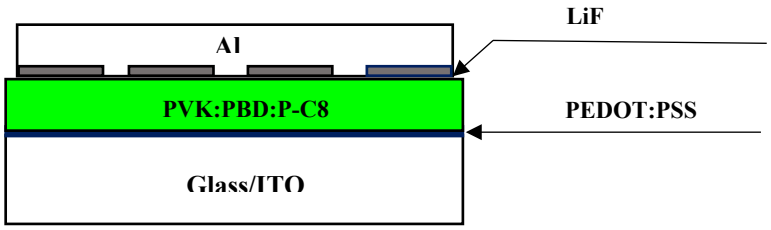
					0.15924
HOTO-1				LUTO+1	

Fabrication and Characterization of OLEDs

In OLEDs fabrication process, the blends of poly(9-vinylcarbazole):2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, **PVK:PBD** (70:30) containing 1 wt% of **P-C8** in chlorobenzene solution were spin coated on top of **indium tin oxide glass substrates** (Ossila), precoated with a **PEDOT:PSS** layer of about 20 nm thickness. The blend layers were *ca.* 70-80 nm thick. In order to remove the residual solvent, the samples were annealed at 90 °C before the cathode deposition. An ultrathin ca. 1 nm **LiF** interfacial layer was evaporated in order to promote electron injection and then covered with a 100 nm thick layer of **aluminum**. The thicknesses of the layers were measured by means of a *DektakXT* profilometer (*Bruker).* The devices had an active area of 0.045 cm^2 (3 x 1.5 mm). The devices prepared in this manner were encapsulated with an epoxy resin and glass inside a glove box. After encapsulation they could be characterized and tested in ambient conditions. The diodes were

electrically characterized using a Keithley 2612 Source-Meter. The electroluminescence spectra were measured using a special collecting optical system and a MicoHR spectrometer with a CCD 3500 detector (Horriba Jobin-Yvon) linked by fiber-optics. This system has flat sensitivity response in the whole wavelength range 350 ÷ 950 nm. A CIE 1931 color coordinates and luminance were recorded using a Minolta CS-200 chromameter.



Scheme S2. The structure of polymer diode built on the base of PVK/PBD/**P-C8**

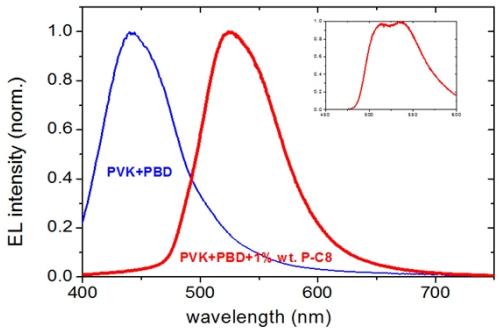


Figure S7. EL spectra of ITO/PEDOT:PSS/**PVK+PBD**/LiF/Al (blue line) and ITO/PEDOT:PSS/**PVK+PBD+P-C8**/LiF/Al (red line). The inset is the high resolution EL spectrum of ITO/PEDOT:PSS/**PVK+PBD+P-C8**/LiF/Al.

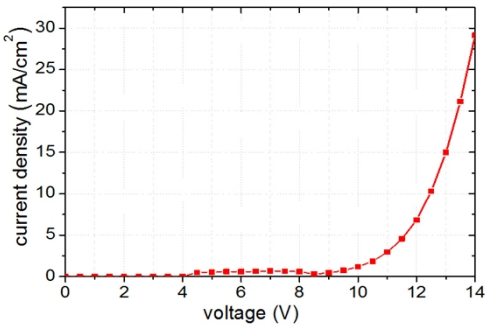


Figure S8. Current density – voltage characteristic of **P-C8 OLED**

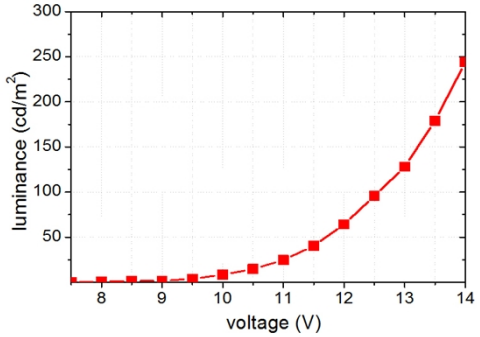


Figure S9. Luminance-voltage characteristic of **P-C8** OLED

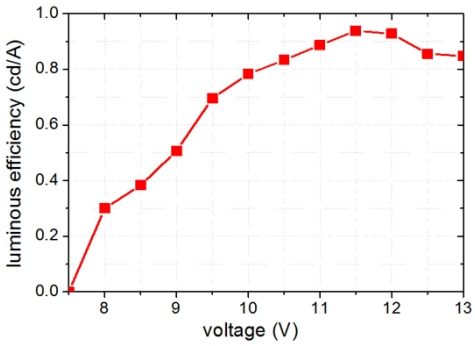


Figure S10. Current efficiency – voltage characteristic of **P-C8** OLED

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