Supplementary Information

Linear and Star-Shaped Naphthalimide fused pyrazinacenes

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Materials and Methods.

NMR spectra were recorded on a Bruker DPX 300, or AV 500 spectrometer at 25 ºC, and the chemical shifts are reported in parts per million using the solvent as reference. The splitting patterns are designated as follows: s = singlet, d = doublet, m = multiplet, bs= broad signal, and the assignments are *Napht* (naphthalene), and *ph* (benzene). Mass spectra were recorded by means of MALDI-TOF and FAB/IE techniques with Bruker Reflex 2 and FAB/IE MAT95 XP Thermofisher mass spectrometers respectively. Melting points were collected in a Nikon eclipse 80i microscope coupled with a Linkam heating plate. Elemental analyses were performed on a Perkin-Elmer EA 2400. UV-Vis spectra were recorded in a Varian Cary 50 spectrometer. FTIR spectra were carried out in a Shimadzu FTIR 8300 spectrophotometer. Optical measurements in solution were carried out in 1 cm cuvettes with Merck Uvasol-grade solvents. Absorption spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer, and corrected fluorescence spectra were recorded on a Perkin-Elmer LS 55 fluorescence spectrometer. TGA and DSC measurements were performed at a heating rate of 10 ºC/min under nitrogen flow on a TA Instruments SDT Q600 and a METTLER TOLEDO DSC822 respectively. Cyclic voltammetry experiments were performed with a computer controlled Autolab

PGSTAT 302 potentiostat in a three electrode single-compartment cell (5 ml). The platinum working electrode consisted of a platinum wire with a surface of A = 0.785 mm^2, which was polished down to 0.5 μm with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was a Ag/AgCl secondary electrode. For solid-state differential pulse voltammetry, the films of **1**-**3**, **7** and *N*,*N*-dioctylnaphthalenediimide were coated on the Pt working electrode by dipping the Pt wire into the solutions of the corresponding compounds in toluene and then drying it in a vacuum oven at 120 °C overnight. An electrolyte solution of 0.1 M $TBAPF_6$ in freshly distilled and degassed acetonitrile (HPLC, Aldrich) was used in all experiments.

UV/Vis absorption spectra were recorded in 1 cm cuvettes with Merck Uvasol grade solvents on a Perkin Elmer Lambda 19 spectrometer. Fluorescence spectra were recorded on a Perkin Elmer LS-55 luminescence spectrometer. The fluorescence spectra are fully corrected for monochromator and photomultiplier artifacts.

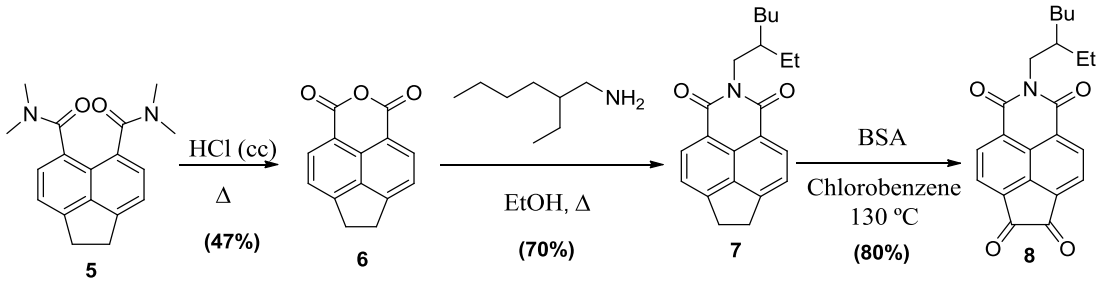
Density functional theory (DFT) was employed with the hybrid functional B3LYP and the basis set 6-31G+ including d and p diffuse functions from the Gaussian 09 package. The long butyl/ethyl chains, which have no significant impact on the frontier orbitals of the chromophores, were replaced with ethyl substituents in order to accelerate the convergence of optimizations.

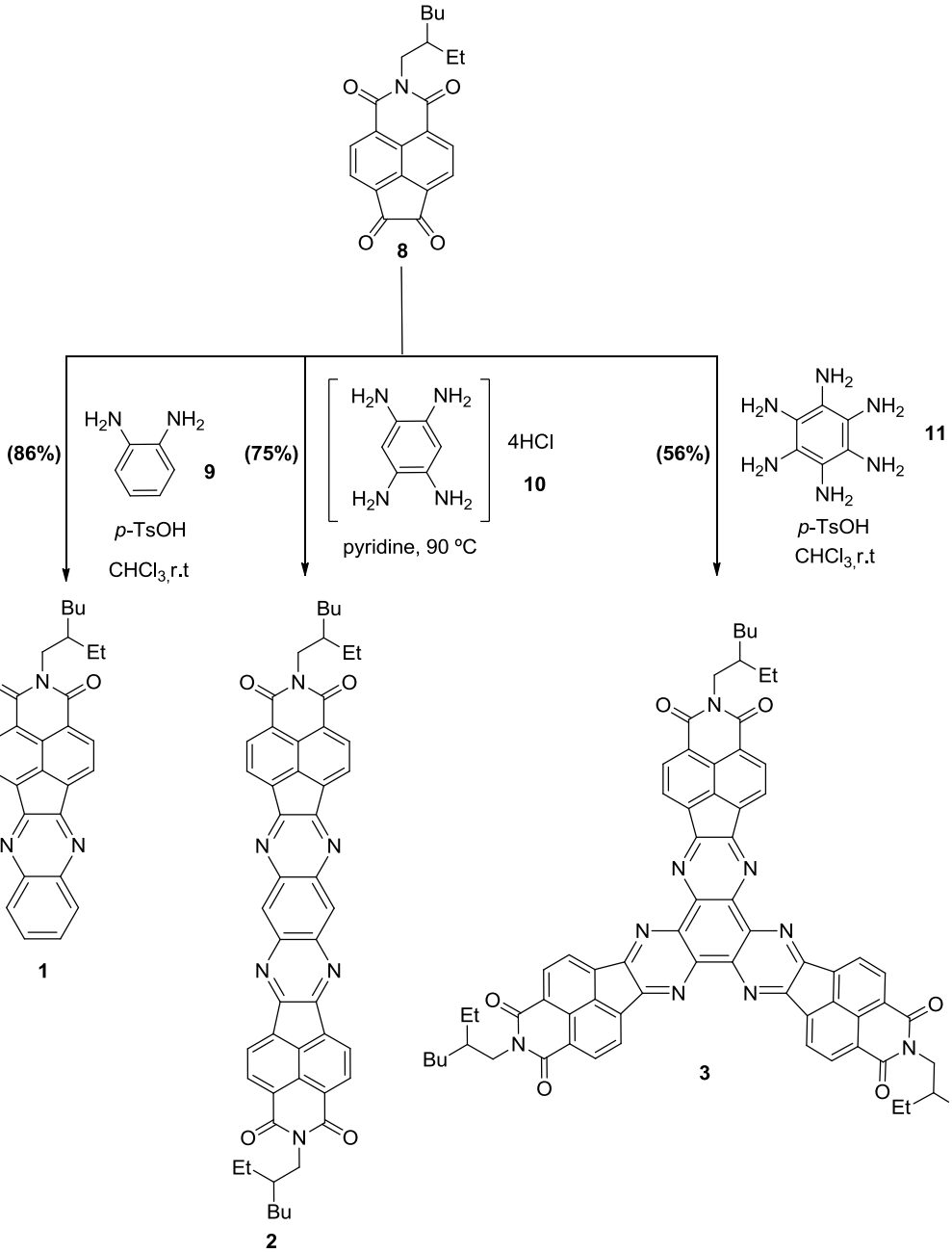
The Surface images were recorded with the help of a Bruker Nanoscope V AFM at ambient temperature in the tapping mode. For the deposition, the compounds were spin-coated on Si/SiO_2 wafer at 2000 rpm during 300 s from $3 \cdot 10^{-4}$ M solutions. The solvent was DCM in the case of compound **1**, and toluene for cases **2** and **3**. For compound **2**, the spin-coating process started 30 s after the deposition of the droplet.

Materials:

Diamide **5**[1] and benzene-1,2,3,4,5,6-hexaamine **11**[2] were prepared according to the literature procedures. All other chemicals were purchased from Aldrich and used as received without further purification.

The synthetic procedures are shown in the schemes below.





Synthesis of 6,7-dihydroindeno[6,7,1-def]isochromene-1,3-dione (**6**)

Diamide **5** (517 mg, 1.74 mmol) was suspended in 7 mL of HCl (cc). The suspension was heated at 60 ºC during 3.5 h. Then, the precipitate formed was filtered, washed with water and dried. Finally, the solid was purified by column chromatography (silica gel flash, dichloromethane) to yield 183 mg (47%) of **6** as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.50 (d, *J* = 7.4 Hz, 2H, *Napht*), 7.61 (d, *J* = 7.4 Hz, 2H, *Napht*), 3.61 (s, 4H, CH_2-CH_2).

^{13}C-NMR (75MHz, $CDCl_3$) δ = 164.1, 160.9, 155.7, 134.9, 121.6, 115.6, 32.0.

FTIR (ATR, CH_2CL_2), υ (cm^{-1}) = 3085, 2924, 2854, 2362, 1778, 1738, 1659, 1626, 1503, 1450, 1410, 1297, 1230, 1201, 1152, 1114, 1091, 1042, 982, 946, 859, 828, 793, 758, 714, 680, 638.

MS (EI): (*m/z*) = 224 (M^+)

Anal;calculated for $C_{14}H_8O_3$: C, 75.00 %; H, 3.60 %; found: C, 74.67 %; H, 3.68 %.

M.p.: 270ºC

Synthesis of 2-(2-ethylhexyl)-6,7-dihydro-1H-indeno[6,7,1-def]isoquinoline-1,3(2H)-dione (**7**).

Compound **6** (183 mg, 0.82 mmol) was suspended in 7 mL of absolute ethanol under argon atmosphere. The mixture was refluxed. After one hour 2-ethylhexylamine (0.16 ml, 0.98 mmol) was added dropwise to the mixture. The reaction was refluxed overnight. Then the reaction was cooled to room temperature, the solvent was removed by rotary evaporation and the residue solid was solved in dichloromethane. The solution was washed twice with water. The organic layer was dried under $MgSO_4$ and the solvent was removed under reduced pressure. The solid was purified by column chromatography (silica gel flash, dichloromethane) to yield 192 mg (70 %) of **7** as a yellow solid.

^{1}H RMN (300 MHz, $CDCl_3$) δ = 8.48 (d, *J* = 7.3 Hz, 2H, *Napht*), 7.55 (d, *J* = 7.3 Hz, 2H, *Naphth*), 4.19-4.05 (m, 2H), 3.56 (s, 4H, CH_2-CH_2), 1.99 - 1.87 (m, 1H, CH), 1.43 – 1.23 (m, 8H, CH_2), 0.95-0.84 (m, 6H, CH_3).

^{13}C RMN (75 MHz, $CDCl_3$) δ = 164.9, 153.9, 137.9, 132.9, 126.6, 121.0, 119.4, 44.2, 38.2, 31.8, 31.0, 28.9, 24.3, 23.2, 14.2, 10.9.

FTIR (ATR, CH_2CL_2), υ (cm^{-1}) = 2958, 2928, 2859, 1694, 1659, 1631, 1450, 1415, 1381, 1334, 1237, 1173, 1116, 1068, 975, 857, 831, 771, 727, 663, 641.

MS (MALDI TOF): (*m/z*) = 335.8 (M^+)

Anal.; calculated for $C_{22}H_{25}NO_2$: C, 78.77%; H, 7.51%; N, 4.18 %; FoundC, 77.59 %; H, 7.40 %; N, 4.16 %.

m.p.: 142-143º

Synthesis of 2-(2-ethylhexyl)-1H-indeno[6,7,1-def]isoquinoline-1,3,6,7(2H)-tetraone (8):

Over a solution of imide **7** (0.670 g, 1.99 mmol) in 35 mL of chlorobenzene, benzeneseleninic acid anhydride (BSA) (2.3 g, 4.37 mmol) was added. The mixture was heated at 130º during 48 hours. Then the solvent was removed, the solid was dissolved in dichloromethane and washed with water twice. The organic layer was dried with magnesium sulfate and the solvent was removed by rotary evaporation. The solid was purified by column chromatography (silica gel flash, dichloromethane) to yield 570 mg (80 %) of **8** as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.80 (d, *J* = 7.3 Hz, 2H, *Napht*), 8.34 (d, *J* = 7.3 Hz, 2H, *Napht*), 4.22-4.09 (m, 2H), 1.97-1.89 (d, 1H), 1.43-129 (m, 8H), 0.96-0.85 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 186.4, 163.0, 143.9, 132.3, 126.9, 126.4, 123.0, 44.9, 38.1, 30.9, 28.8, 24.2, 23.2, 14.2, 10.8.

FTIR (ATR, CH_2CL_2), υ (cm^{-1}) = 3072, 2960, 2927, 2860, 1743, 1706, 1670, 1624, 1588, 1455, 1373, 1327, 1234, 1171, 1146, 1119, 1059, 985, 876, 824, 754, 725.

MS (FAB): (*m/z*) = 364.2 (M+1)

Anal.: calculated for $C_{22}H_{21}NO_4$: C, 72.71 %; H, 5.82 %; N, 3.85 %; Found: C, 70.99 %; H, 5.76 %; N, 3.93 %.

M.p.: 180-182 ºC

Synthesis of quinoxaline-naphthalimide derivative (1):

Over a solution of *o*-phenylenediamine (**9**) (24 mg, 0.22 mmol) in dry chloroform, dione **8** (80mg, 0.22 mmol) and a catalytic amount of *p*-toluenesulfonic acid were added under argon atmosphere. The mixture was kept at room temperature overnight. The product was precipitated in methanol, the precipitated was filtered under vacuum and washed with methanol. Finally, the solid was purified by column chromatography (silica gel flash, dichloromethane) to yield 82 mg (86 %) of **1** as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.72 (d, *J* = 7.3 Hz, 2H, *Napht*), 8.51 (d, *J* = 7.3 Hz, 2H, *Napht*), 8.23 (m, 2H, *Ph*), 7.83 (m, 2H, *Ph*), 4.17 (m, 2H), 1.96 (m, 1H), 1.38 (m, 8H), 0.93 (m, 6H).

^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 163.7, 154.1, 141.3, 136.8, 134.8, 132.6, 130.5, 130.1, 125.2, 124.3, 122.5, 53.5, 44.3, 38.2, 30.8, 28.7, 24.1, 23.1, 14.2, 10.7.

MS (FAB) (m/z): 436.18 $[M+1]^+$

FTIR (ATR), ν (cm^{-1})= 2956, 2927, 2864, 1741, 1706, 1461, 1323, 1231, 758.

Anal: calculated for $C_{28}H_{25}N_3O_2$: C 77.22%, H 5.79%, N 9.65%, Found: C 77.31 %, H 6.08%, N 9.79%.

Synthesis of pyrazino[2,3-g]quinoxaline-bisnapthalimide derivative (2):

Under argon atmosphere, a mixture of dry and degassed pyridine (5 mL), 1,2,4,5-benzenetetramine tetrahydrochloride (**10**, 31 mg, 0.11 mmol) and dione **8** (80 mg, 0.22 mmol) was heated at 90 ºC overnight. Then, the precipitated was filtered under vacuum and washed with hexane, dichloromethane and methanol to yield 65 mg (75 %) of **2** as an orange solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 9.61 (s, 2H, *Ph*), 8.93 (d, *J* =7.3 Hz, 4H, *Napht*), 8.81 (d, *J* =7.3 Hz, 4H, *Napht*), 4.23 (m, 4H), 1.96 (m, 2H), 1.55-1.18 (m, 16H), 0.93 (m, 12H).

^{13}C-RMN (300 MHz, $CDCl_3$) δ = 166.0, 156.3, 138.7, 138.6, 135.0, 133.5, 128.0, 127.3, 126.4, 126.1, 46.5, 38.9, 31.0, 28.9, 24.2, 23.1, 13.0, 9.7.

MS (FAB) (m/z): 793.9 $[M+1]^+$

FTIR (ATR), ν (cm^{-1})= 2958, 2871, 1704, 1667, 1454, 1327, 1235, 1180. 880, 755

Anal: calculated for $C_{50}H_{44}N_6O_4$: C 75.74 %, H 5.59 %, N 10.60 %, Found: C 75.57 %, H 5.62 %, N 10.06 %.

Synthesis of hexaazatriphenylene-trisnapthalimide derivative (3):

Under argon atmosphere, benzene-1,2,3,4,5,6-hexaamine (**11**, 30 mg, 0.18 mmol) was solved in dry chloroform (12mL). Over the solution, dione **8** (200 mg, 0.55 mmol) and a catalytic amount of *p*-toluenesulfonic acid were added. The mixture was kept at room temperature overnight. The crude was filtered under vacuum and was washed with dichloromethane and hexane. The solid was purified by vacuum sublimation to yield 117 mg (56 %) of **3** as a green solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.84 (d, *J* = 7.3 Hz, 6H, *Napht*), 8.75 (d, *J* = 7.3 Hz, 6H, *Napht*), 4.23 (m, 6H), 1.96 (m, 3H), 1.40 (m, 24H), 0.94 (m, 18H).

^{13}C-RMN (300 MHz, $CDCl_3$) δ = 165.8, 156.8, 138.9, 135.5, 135.2, 135.1, 134.6, 126.6, 125.6, 46.2, 38.7, 30.8, 28.7, 24.0, 22.9, 12.7, 9.5.

MS (FAB) (m/z): 1151.49 $[M+1]^+$

FTIR (ATR), ν (cm^{-1})= 2955, 2867 1706, 1668, 1635, 1591, 1150, 1375, 1330, 1238, 1178, 1075, 822, 619.

Anal: calculated for $C_{72}H_{63}N_9O_6$: C 75.18 %, H 5.52 %, N 10.96 %, Found: C 75.66 %, H 5.63 %, N 10.92 %.

References

B. M. Trost, G. M. Bright, C. Frihart, D. Britelli, *J. Am. Chem. Soc.* **1971**, *93*, 737

D.Z. Rogers, *J. Org. Chem.* **1986**, *51*, 3904.

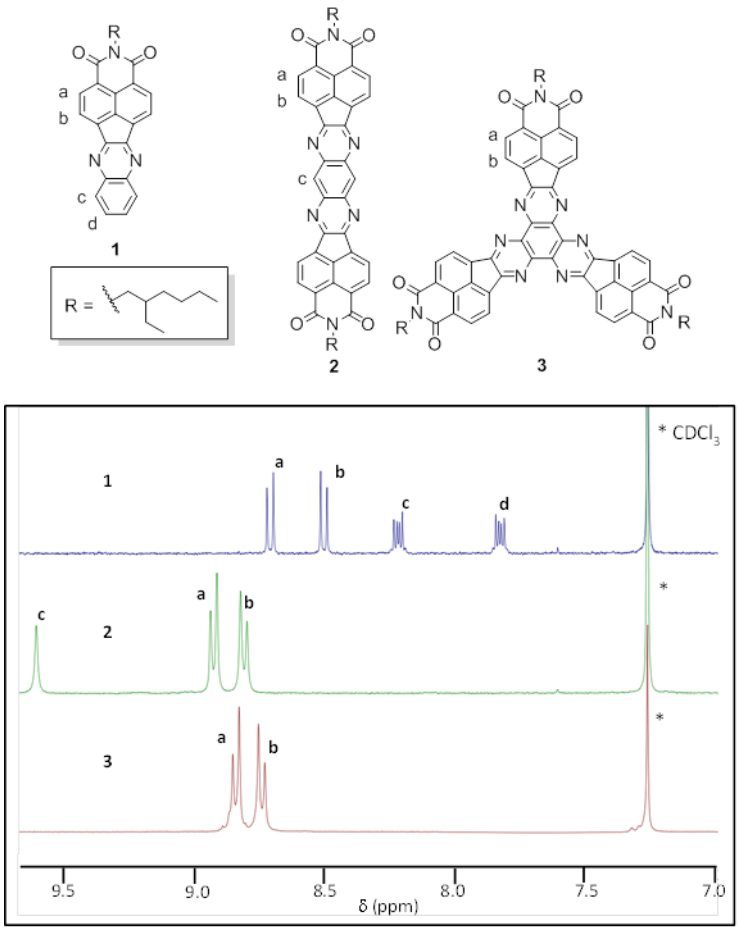


Figure S1. Aromatic regions of the 1H-NMR spectra of **1**,**2** and **3** measured in CDCl3/CF3COOD. The resonances were assigned to the corresponding protons shown in the chemical structures represented above.

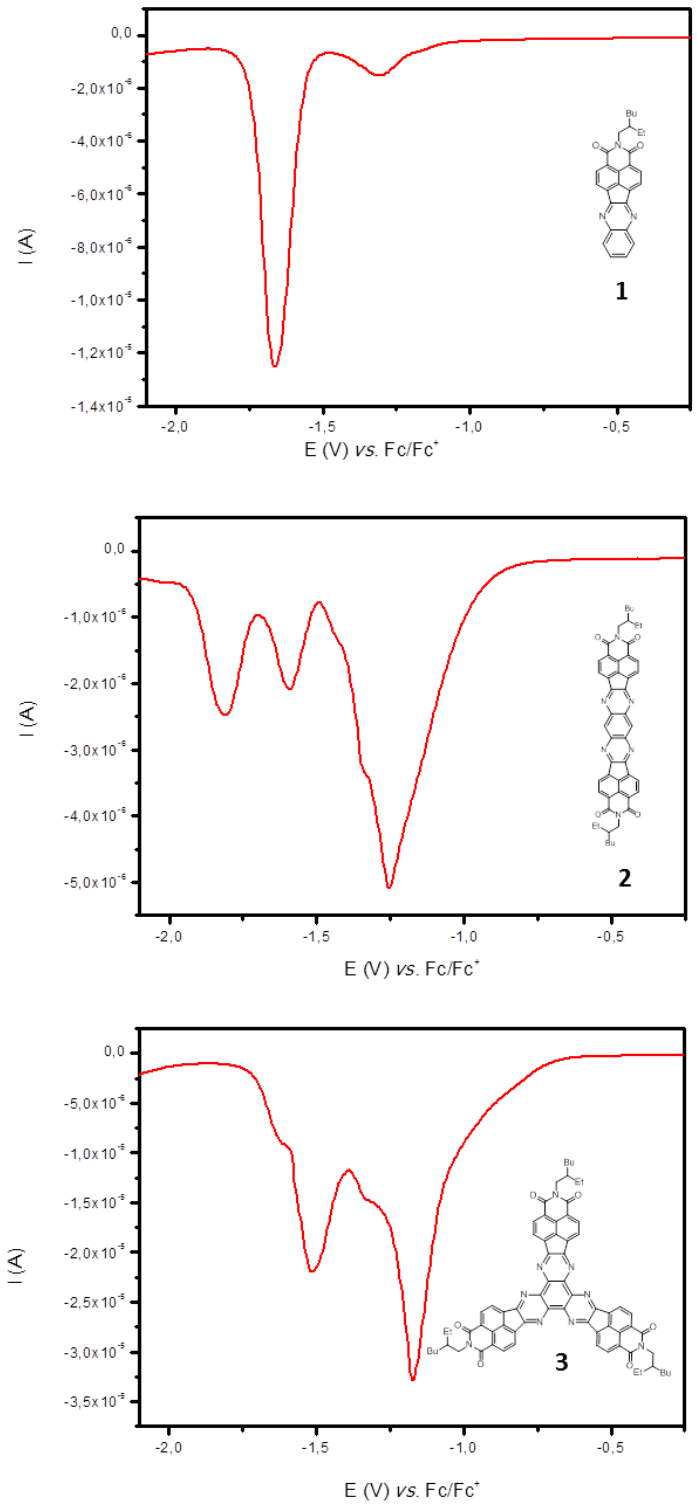
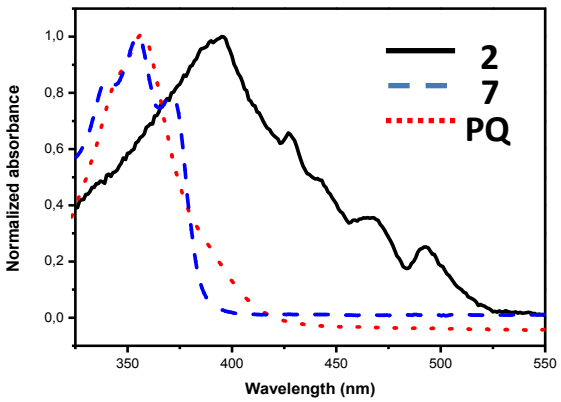
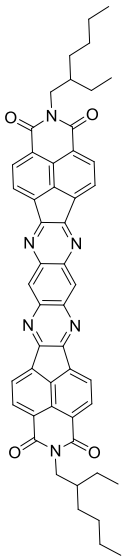
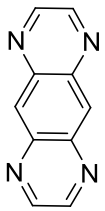
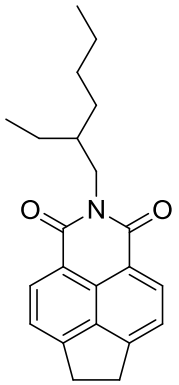


Figure S2. Differential pulse voltammograms of thin films of **1** (top), **2** (middle) and **3** (bottom). An electrolyte solution of 0.1 M TBAHPF in acetonitrile as used. Platinum electrodes were used as both counter and working electrodes. Ag/Ag^+ was used as the quasi referencre electrode and the potentials were referenced to the couple Fc/Fc^+ .









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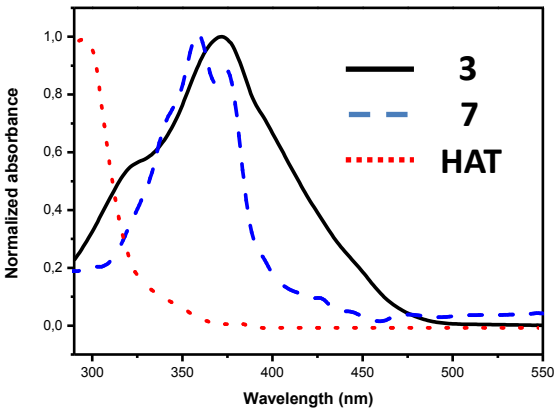

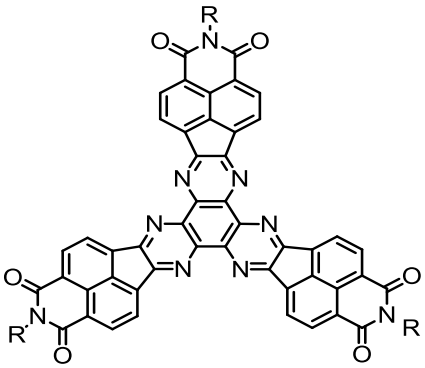

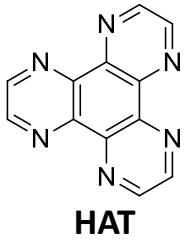

HAT

3

Figure S3. Normalized UV-vis absorption spectra of **2** together with that of references **7** and **PQ** (top) and **3** together with that of references **7** and **HAT** (bottom). All spectra were carried out in toluene solutions.

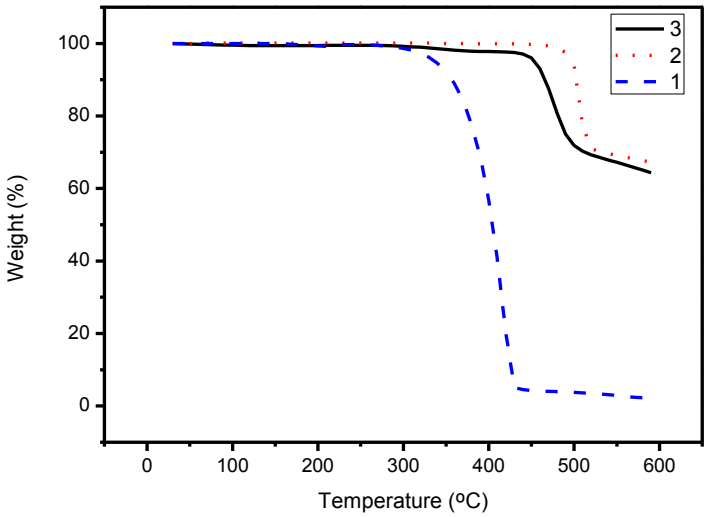

Figure S4. The thermal stability was determined by using thermogravimetric analysis (TGA) in nitrogen gas at a heating rate of 10 °C/min. The decomposition temperatures (T_d, corresponding to the 5% weight loss) for compounds **1, 2** and **3** are at 340, 460 and 500 °C.

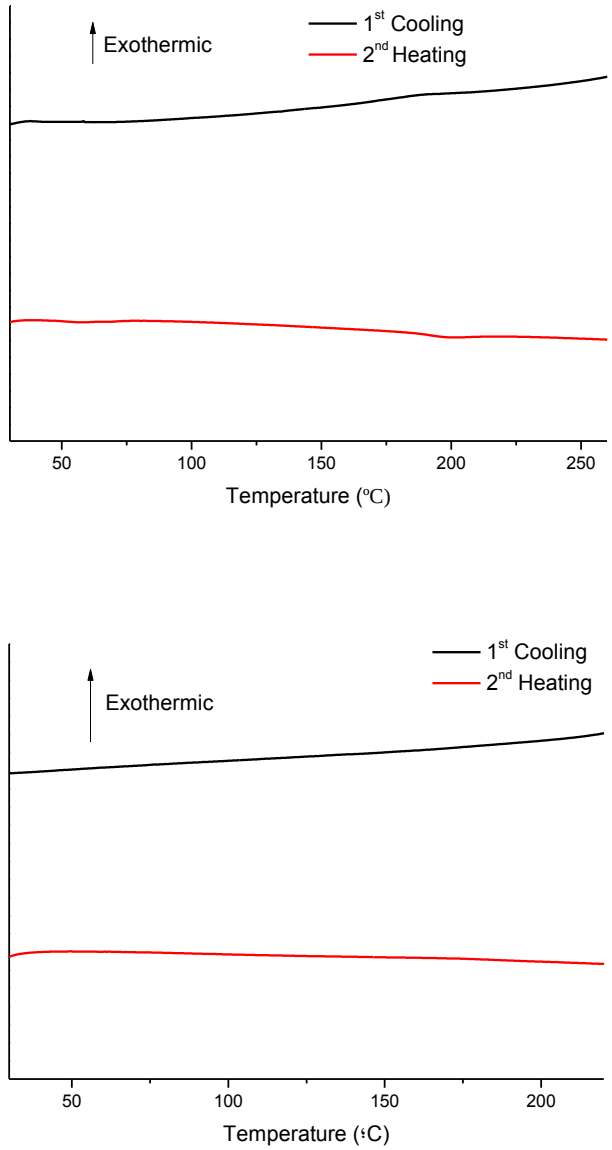

Figure S5. Differential scanning calorimetry (DSC) curves of compunds **2** (top) and **3** (bottom) at a heating rate of 10 °C/min showing no phase transition.

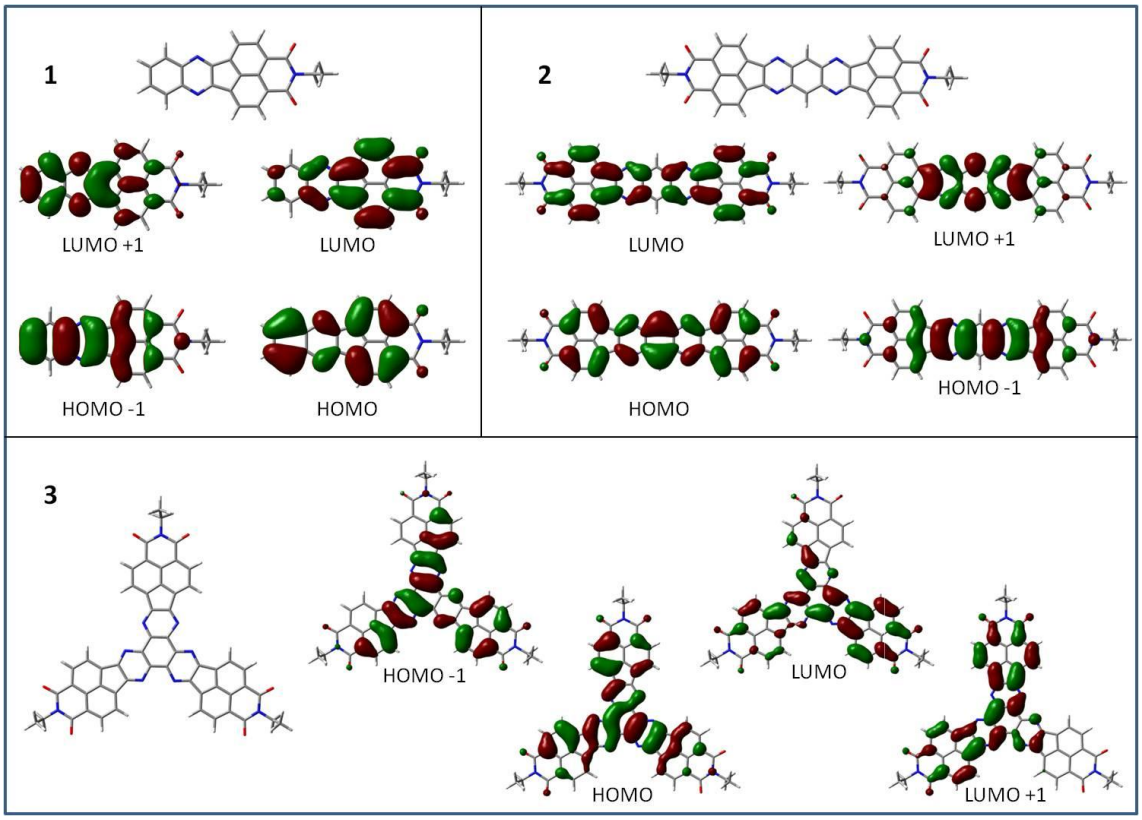

Figure S6. Representation of the frontier molecular orbitals HOMO, HOMO-1, LUMO and LUMO+1 obtained from DFT calculations for compounds **1-3**.