

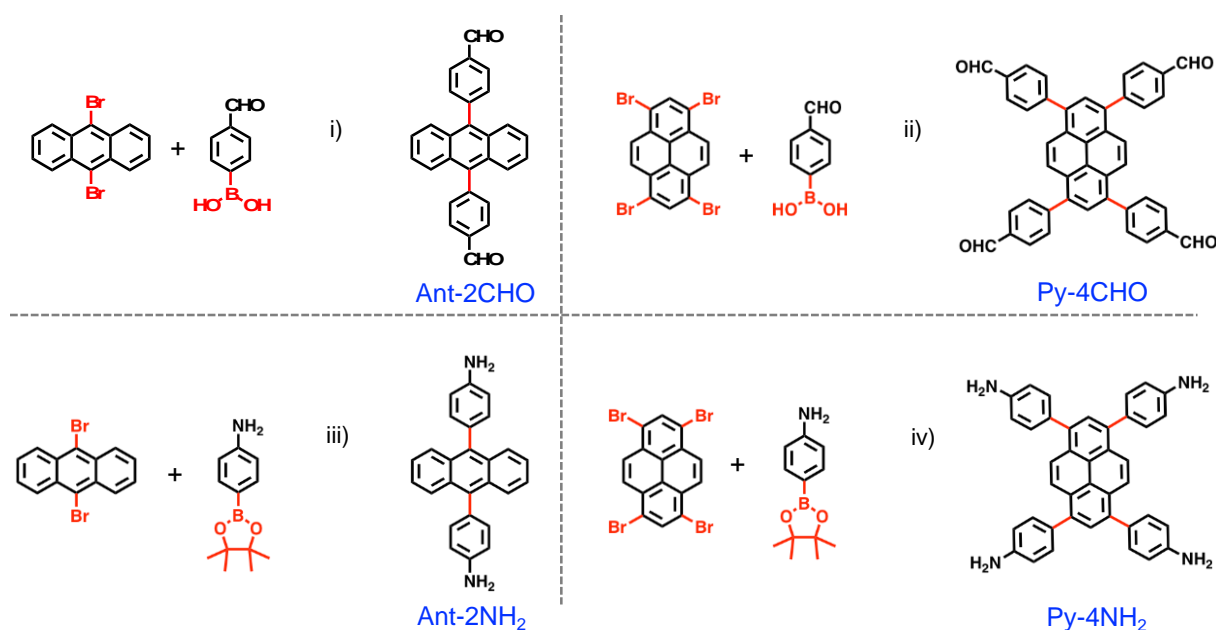
Supplementary Information for

Impact of the Position of Imine-Linker over Optoelectronic Performance of π -Conjugated Organic Frameworks

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1. Scheme for the Synthesis of the Building blocks



Scheme 1. Reagents and conditions: i) K₂CO₃, Pd(PPh₃)₄, Toluene:Ethanol:Water (5:1:2), reflux, 48 h; ^{S1,S2} ii) K₂CO₃, Pd(PPh₃)₄, Dioxane, reflux, 72 h; ^{S3} iii) Na₂CO₃, Pd(PPh₃)₄, Dioxane:Water (4:1), reflux, 48 h; iv) K₂CO₃, Pd(PPh₃)₄, Dioxane:Water (4:1), reflux, 72 h. ^{S4}

9,10-bis(4-formylphenyl)anthracene (Ant-2CHO).

Yield = 84%, pale yellow powder.

^1H NMR (400 MHz, CDCl_3): δ = 10.20 (2H, s, ArCHO), 8.14 (4H, d, ArH), 7.68 (4H, d, ArH), 7.62 (4H, d, ArH), 7.37 (4H, d, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 191.9 (ArCHO), 145.7, 136.2, 135.8, 132.1, 129.8, 129.4, 126.5, 125.7.

MALDI-TOF MS for $\text{C}_{28}\text{H}_{18}\text{O}_2$: $[\text{M}]^+$ found 385.35, calculated 386.13.

1,3,6,8-tetrakis(4-formylphenyl)pyrene (Py-4CHO).

Yield = 70%, bright yellow powder.

^1H NMR (400 MHz, CDCl_3): δ = 10.14 (2H, s, ArCHO), 8.16 (4H, d, ArH), 8.06 (8H, d, ArH), 8.02 (2H, s, ArH), 7.85 (8H, d, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 192.0 (ArCHO), 146.8, 136.5, 135.6, 131.4, 129.9, 128.5, 125.8.

MALDI-TOF MS for $\text{C}_{44}\text{H}_{26}\text{O}_4$: $[\text{M}]^+$ found 618.08, calculated 618.18.

9,10-bis(4-aminophenyl)anthracene (Ant-2NH₂).

Yield = 60%, bright greenish yellow powder.

^1H NMR (400 MHz, CDCl_3): δ = 7.79 (4H, m, ArH), 7.30 (4H, m, ArH), 7.23 (4H, d, ArH), 6.91 (4H, d, ArH), 3.83 (4H, s, ArNH₂).

^{13}C NMR (100 MHz, CDCl_3): δ = 145.6, 137.0, 132.2, 130.4, 129.0, 127.1, 124.6, 115.0.

MALDI-TOF MS for $\text{C}_{26}\text{H}_{22}\text{N}_2$: $[\text{M}]^+$ found 359.2, calculated 360.16.

1,3,6,8-tetrakis(4-aminophenyl)pyrene (Py-4NH₂).

Yield = 75%, bright yellow powder.

^1H NMR (400 MHz, d_8 -THF): δ = 9.95 (4H, s, ArH), 9.65 (2H, s, ArH), 9.16 (8H, d, ArH), 8.56 (8H, d, ArH), 6.25 (8H, s, ArNH₂).

^{13}C NMR (100 MHz, d_8 -Acetone): δ = 169.4, 152.2, 138.5, 138.1, 136.1, 132.0, 130.4, 128.7, 126.0.

MALDI-TOF MS for $C_{40}H_{30}N_4$: $[M]^+$ found 566.02, calculated 566.25.

2. Syntheses of CMPs

2.1. Synthesis of C-AntPy

Py-4NH₂ (37 mg, 65.34 μ mol, 1 eq.) and **Ant-2CHO** (51 mg, 131.97 μ mol, 2 eq.) were dissolved in 8 mL dry dioxane by sonication. To this mixture, a solution of Scandium(III) trifluoromethanesulfonate (2.6 mg, 5.2 μ mol) was added, and the resulting suspension was gently sonicated to ensure proper mixing. This leads to an immediate formation of a colloidal suspension which was kept undisturbed for 6 hours for maximum conversion. An orange precipitate was obtained which was washed several times with dioxane, acetone, methanol (MeOH) and tetrahydrofuran (THF). Further, the precipitate was washed with THF using a Soxhlet extractor for 24 h to remove unreacted monomers as well trace amounts of metal catalyst. The precipitate was dried at 100 °C, yielding a bright yellow fluffy powder.

2.2. Synthesis of N-AntPY

Ant-2NH₂ (11.6 mg, 32.18 μ mol, 2 eq.) and **Py-4CHO** (10 mg, 16.17 μ mol, 1 eq.) were dissolved in 3 mL dry dioxane by sonication. To this mixture a solution of Scandium(III) trifluoromethanesulfonate (0.8 mg, 1.6 μ mol) was added, and the resulting suspension was gently sonicated to ensure proper mixing and kept it undisturbed for 8 hours. An yellow orange precipitate was obtained which was washed several times with dioxane, acetone, methanol (MeOH) and tetrahydrofuran (THF). Further, the precipitate was washed with THF using a Soxhlet extractor for 24 h to remove unreacted monomers as well trace amounts of metal catalyst. The precipitate was dried at 100 °C, yielding a dark yellow fluffy powder.

3. Description of Experimental Techniques

Flash–Photolysis Time Resolved Microwave Conductivity (FP–TRMC)

A resonant cavity was used to obtain a high degree of sensitivity in the conductivity measurements. The resonant frequency and microwave power were set at ~ 9.1 GHz and 3 mW, respectively, so that the electric field of the microwave was sufficiently small not to disturb the motion of charge carriers. The third harmonic generation (THG; 355nm) of a Nd:YAG laser (Continuum Inc., Surelite II, 5 –8 ns pulse duration, 10 Hz) was used as an excitation source. The laser power was fixed at $2.5 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ for all excitation wavelengths (incident photon density, $I_0 = 4.6 \times 10^{15} \text{ photons cm}^{-2} \text{ pulse}^{-1}$). An in–house–built Xe–flash lamp (10 μs pulse duration, 10 Hz) with a power of $0.3 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ was used for the Xe–flash TRMC experiments. For the attenuation of excitation light energy, neutral density filters were used for both Xe–flash and laser–flash TRMC. In the case of laser–flash TRMC, the photoconductivity transient $\Delta\sigma$ is converted to the product of the quantum efficiency: ϕ and the sum of charge carrier mobilities, $\Sigma\mu$, by $\phi\Sigma\mu = \Delta\sigma (eI_0F_{\text{light}})^{-1}$, where e and F_{light} are the unit charge of a single electron and a correction (or filling) factor.

4. Additional Figures

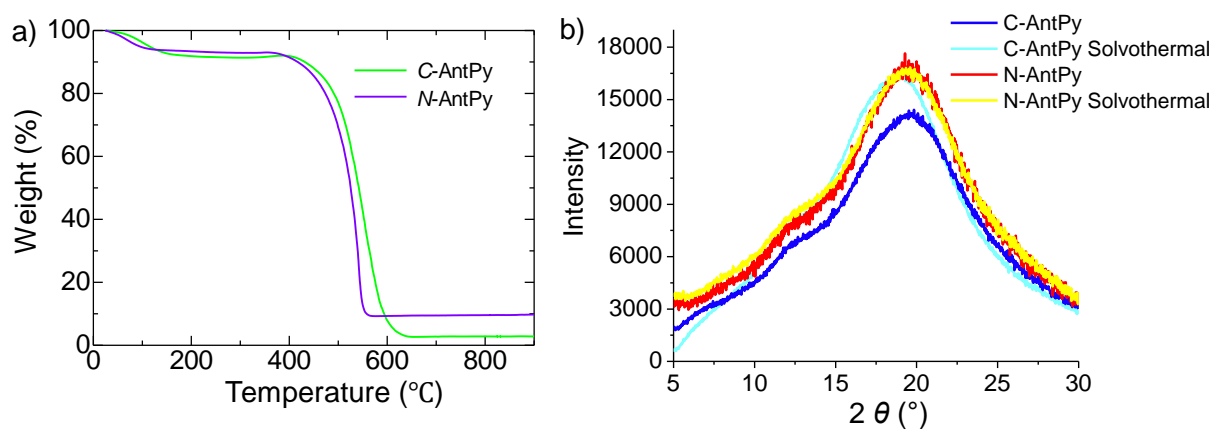


Fig. S1 (a) TGA and (b) PXRD of **C-AntPY** and **N-AntPY**.

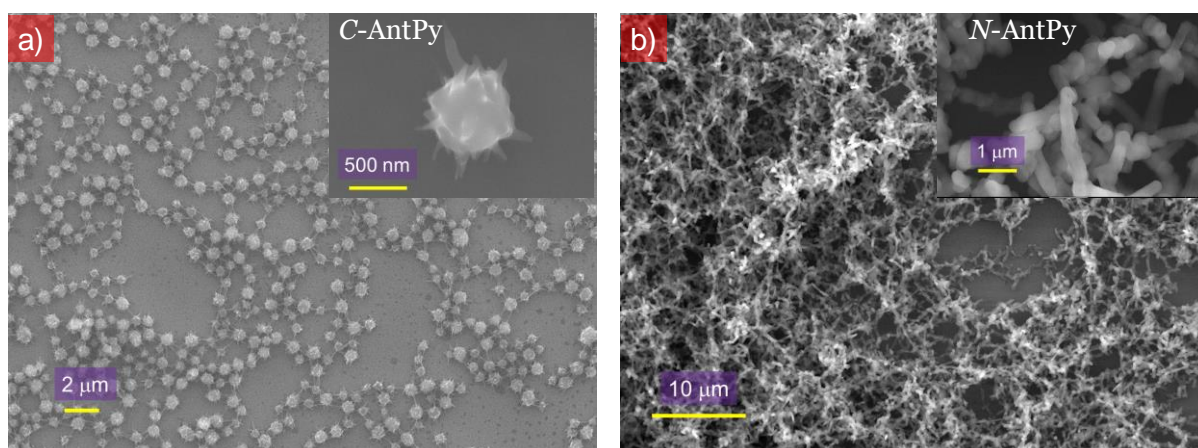


Fig. S2 SEM images of **C-AntPY** and **N-AntPY**.

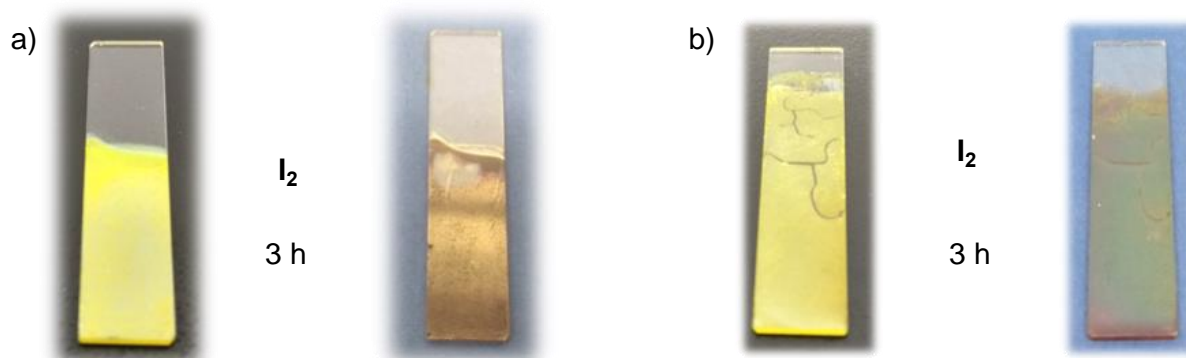


Fig. S3 Thin films of (a) **C-AntPY** and (b) **N-AntPY** before and after I_2 doping.

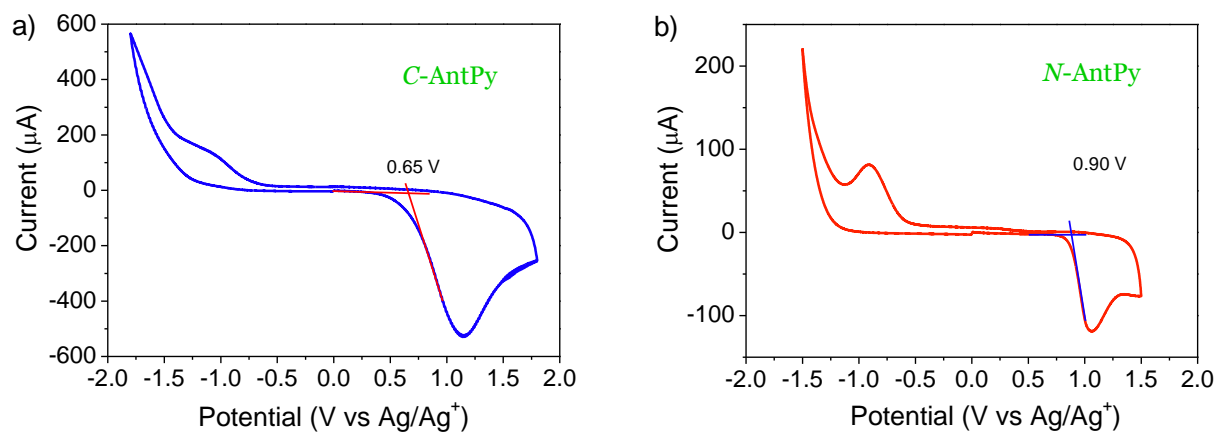


Fig. S4 Cyclic Voltammetry of **C-AntPY** and **N-AntPY** in their film state using ferrocene as the internal standard.

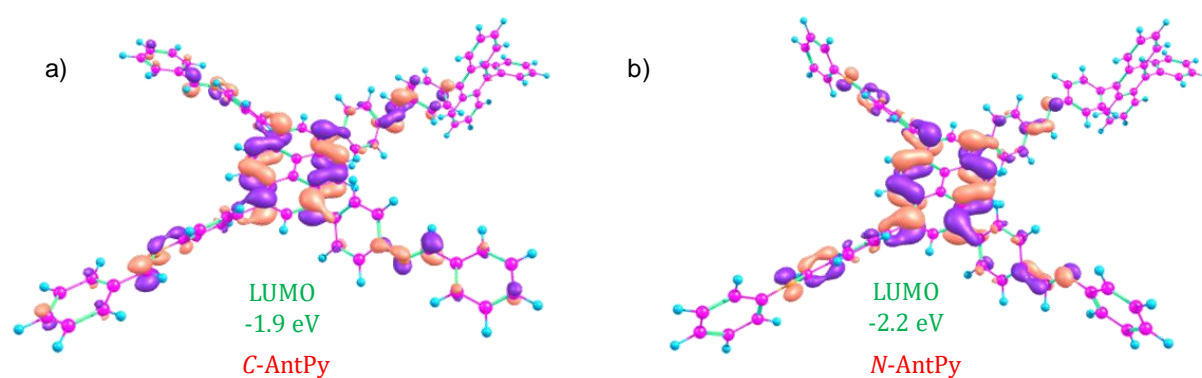


Fig. S5 Frontier orbitals and energy levels of a) **C-AntPy** and b) **N-AntPy**.