Supporting Information

# Pyrene-based Cocrystals for Regulation of Extensive Emission across Visible to Near-infrared II Range

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# Contents

## 1 Experimental

### 1) Materials:

Pyrene (Py, > 98%), tetrafluorophthalonitrile (TFP, > 98%), tetracyanoquinodimethane (TCNQ, > 99%), fluoro-tetracyanoquinodimethane (FTCNQ, > 98%), difluoro-tetracyanoquinodimethane ($F_2$TCNQ, > 98%), tetrafluoro-tetracyanoquinodimethane ($F_4$TCNQ) were purchased from TCI company. Octafluoronaphthalene (OFN, > 96%) and acetonitrile (A.R., > 99.8%) were purchased from Macklin company. Tetrachlorophthalonitrile (TCP, > 98%) and ethanol (A.R., > 99.8%) were purchased from Adamas company. Tetracyanobenzene (TCNB, > 97%) and Octafluoroanthraquinone (OFAQ, > 96%) were purchased from Sigma company. Dichloroanthraquinone (DCAQ, > 97%) was purchased from Shanghai ACMEC company and dinitroanthraquinone (DNAQ, > 96%) was purchased from Jiangsu AIKON company. All of the chemical compounds were directly used without further purification**.**

### 2) Crystals Growth and Characterizations:

Self-assembly of Py-based organic cocrystals: typically, 0.01 mmol Py and 0.01 mmol OFN (and other acceptors) were dissolved in 2 ml acetonitrile (MeCN). The mixed solution was directly dropped onto the glass substrate, and the cocrystals were observed after the solvent evaporated completely.

Preparations of QR codes: typically, 0.1 mmol Py and 0.1 mmol OFN (TCP, TCNB, DNAQ) were dissolved in 10 mL acetonitrile (MeCN). The mixed solution was added dropwise to a glass substrate covered with a mask template. The mask template was removed after the solvent evaporated to obtain the fluorescent QR codes consisting of cocrystals.

One drop of the solution was dropped on a carbon-coated copper grid and evaporated. Transmission electron microscope (TEM) measurement was performed at room temperature at an accelerating voltage of 100 kV. The X-ray diffraction (XRD) patterns were measured by a D/max 2400 X-ray diffractometer with Cu Kα radiation (λ = 1.54050 Å) operated in the 2θ range from 5° to 45°, by using the samples on the quartz. The bright optical images were recorded using a fluorescence optical microscope (Leica, DM4000M, Germany) with a spot-enhanced charge couple device (Diagnostic Instrument, Inc.). The samples were prepared by placing a drop of solution onto a cleaned quartz, and then evaporated at room temperature. Microarea photoluminescence (μ-PL) spectra were collected on a homemade optical microscopy. To measure the PL spectra of the individual crystal, the crystal was excited locally with a 375/532 nm laser focused down to the diffraction limit. The excitation laser was filtered with a 375/532 nm notch filter. The light was subsequently coupled to a grating spectrometer

(Princeton Instrument, ARCSP- 2356) and recorded by a thermal-electrically cooled CCD (Princeton Instruments, PIX-256E). Meanwhile, the time-resolved fluorescence decay of these samples was also measured with a FL-TCSPC spectrofluorimeter (HORIBA Jobin Yvon, French). The absorption spectra were analyzed with a Lambda 950 (varian, USA). The steady-state fluorescence spectra of the samples were measured with a HITACHI F-4600 fluorescence spectrofluorometer at 298 K.

3) **Theoretical Calculations:**

The calculated Bravais Friedel Donnay Harker (BFDH) morphology was shown by Material Studio software and the molecule arrangement was obtained by Mercury software (copyright CCDC)[1,2] according to the crystal structure. Moreover, the energy levels were obtained at the B3LYP/6-31G (d, p) level of theory by Gaussian 09 package.[3]

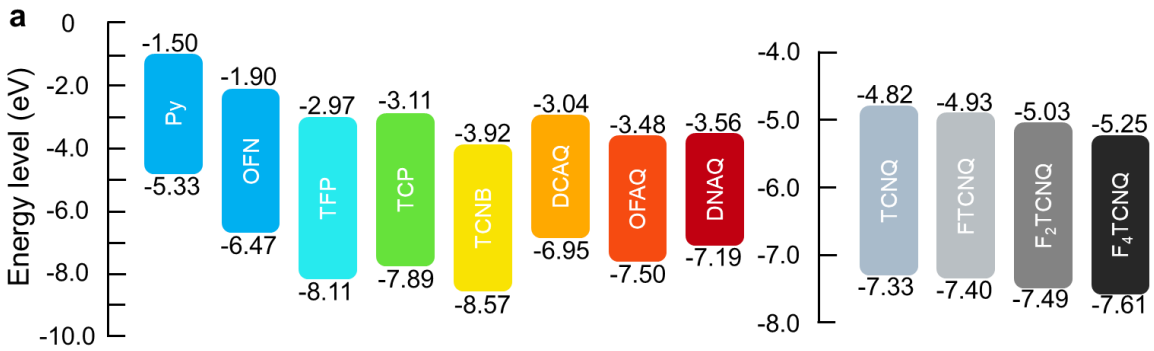


**Figure S1.** a) The energy level of pyrene (Py), octafluoronaphthalene (OFN), tetrafluorophthalonitrile (TFP), tetrachlorophthalonitrile (TCP), tetracyanobenzene (TCNB), dichloroanthraquinone (DCAQ), octafluoroanthraquinone (OFAQ), dinitroanthraquinone (DNAQ), tetracyanoquinodimethane (TCNQ), fluoro-tetracyanoquinodimethane (FTCNQ), difluoro-tetracyanoquinodimethane ($F_2$TCNQ), tetrafluoro-tetracyanoquinodimethane ($F_4$TCNQ).

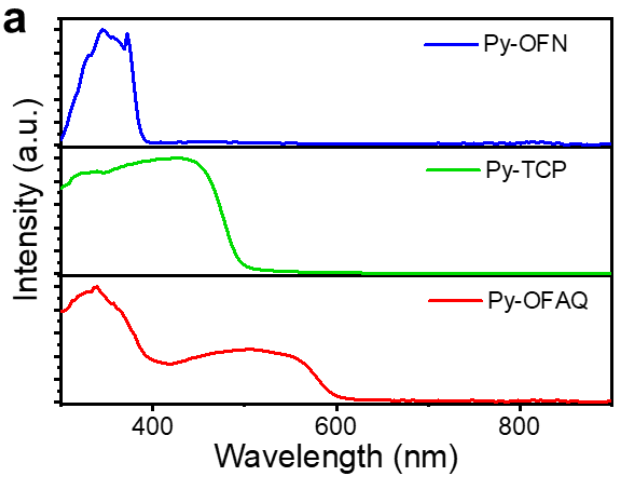


**Figure S2.** a) The absorption spectra of Py-OFN (blue), Py-TCP (green) and Py-OFAQ (red).

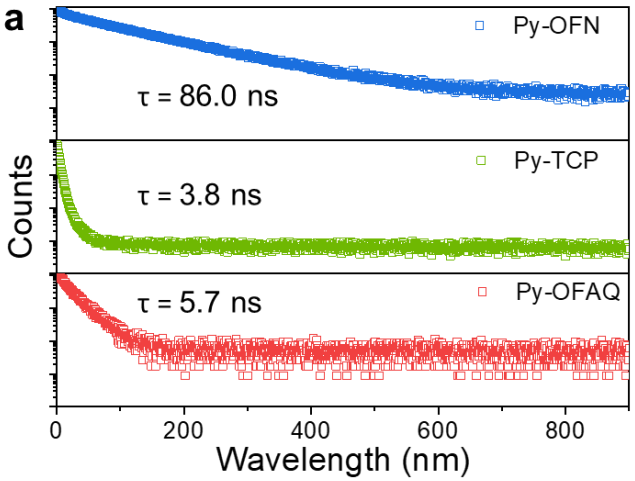


**Figure S3.** The time-resolved fluorescence decay spectrum of Py-OFN, Py-TCP and Py-OFAQ.

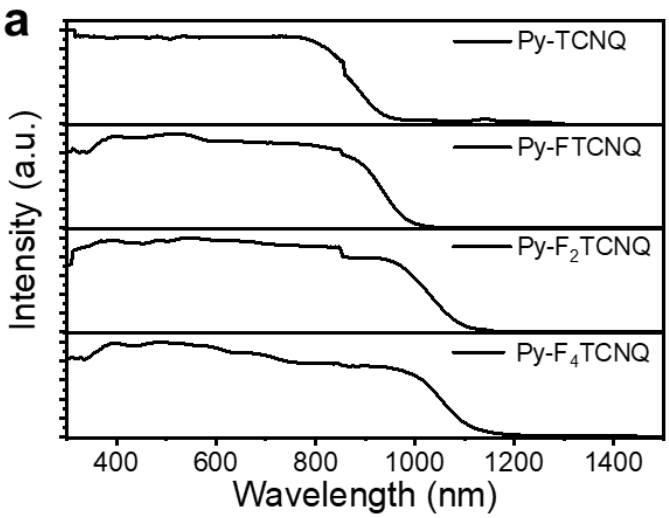


**Figure S4.** a) The absorption spectra of Py-TCNQ, Py- FTCNQ, Py-$F_2$TCNQ and Py- $F_4$TCNQ.

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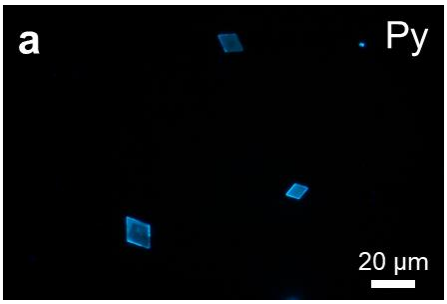


**Figure S5.** a) The fluorescence microscopy (FM) images of pyrene microcrystals.

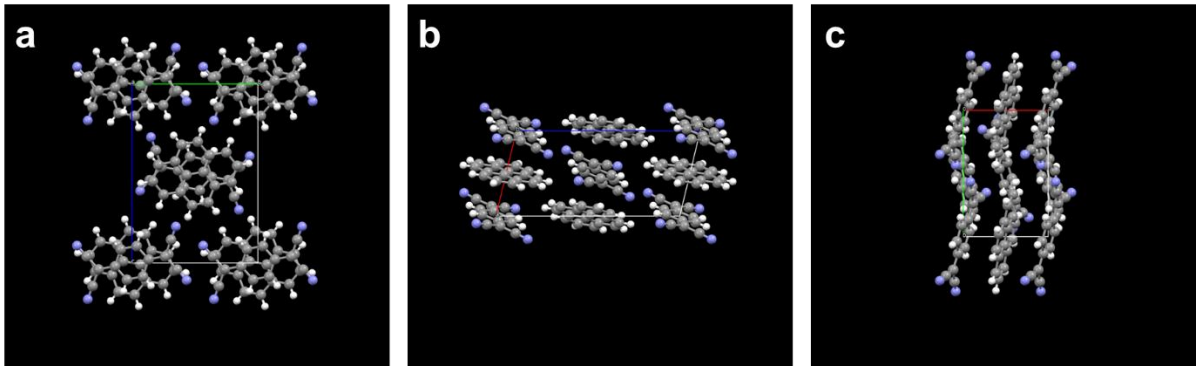


**Figure S6.** The molecular arrangement of the Py-TCNQ cocrystal for a) bc plane, b) ac plane, c) ab plane.

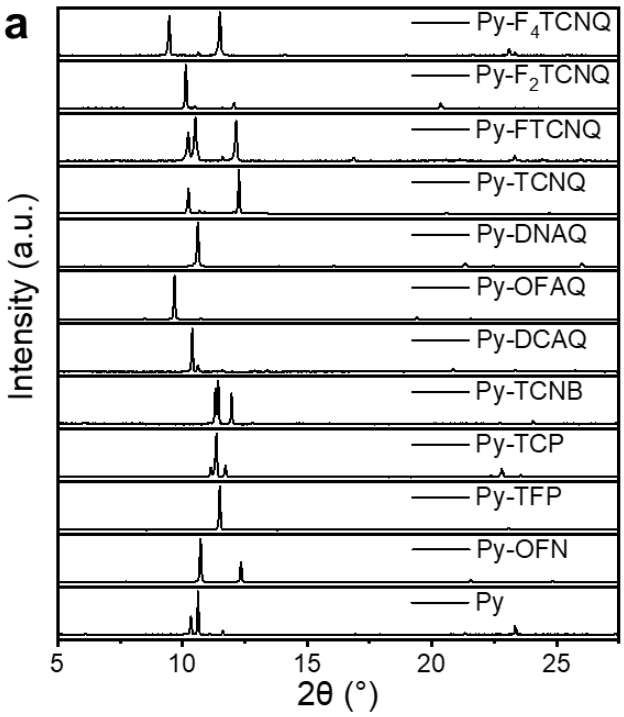


**Figure S7.** The XRD patterns of pyrene crystals and pyrene-based cocrystals.

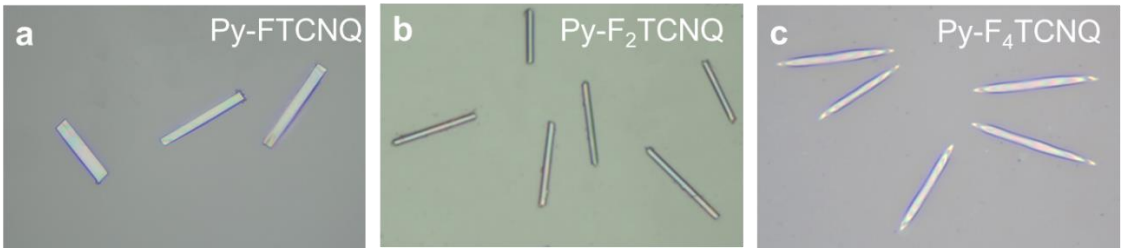


**Figure S8.** The bright-field microscopy images of Py-FTCNQ, Py-$F_2$TCNQ, Py-$F_4$TCNQ.

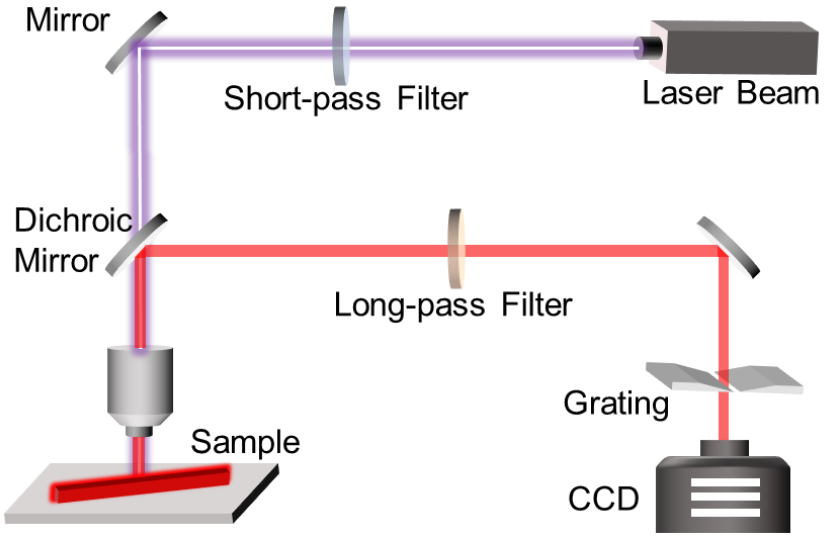


**Figure S9.** Schematic demonstration of the experimental setup for optical characterization. PL microscopy images were taken with an inverted microscope (Olympus, BX43). To measure the PL spectra of the organic microwires, the samples were excited locally with a focused laser beam ($\lambda$ = 375 nm, 532 nm) through an objective (Nikon CFLU Plan, 50×, N.A. = 0.8). The polarization profiles of the emission intensity are obtained by setting a polarizer in front of the detector. The emission from the tip of the microwires is dispersed with a grating (150 G/mm) and recorded with a thermal-electrically cooled CCD (Princeton Instruments, PIX-256E).

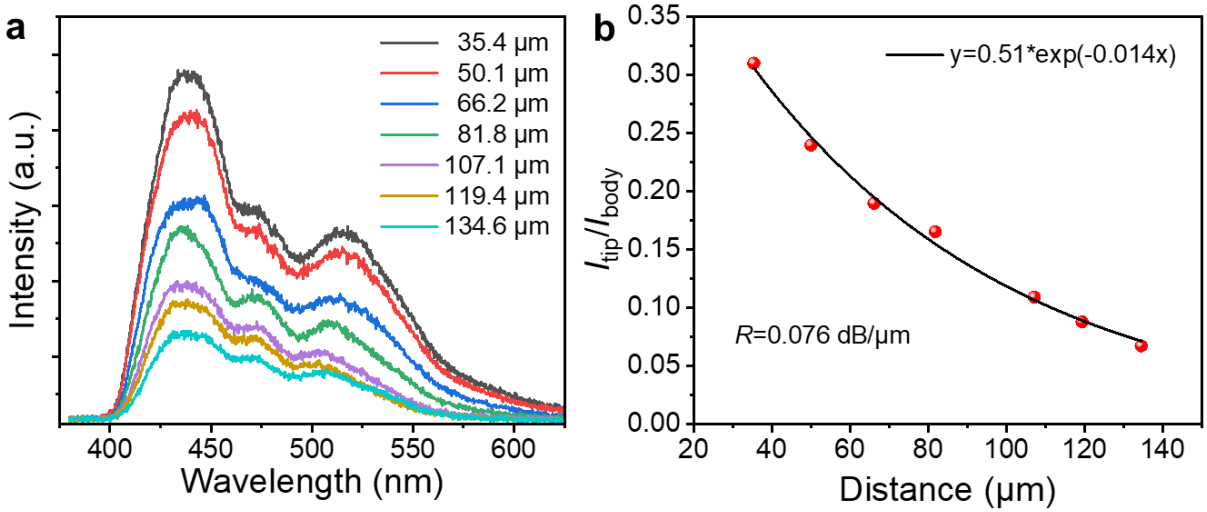


**Figure S10.** a) The spatially resolved PL spectra of Py-OFN and b) their curve of intensity $I_{tip}/I_{body}$ with distance D.

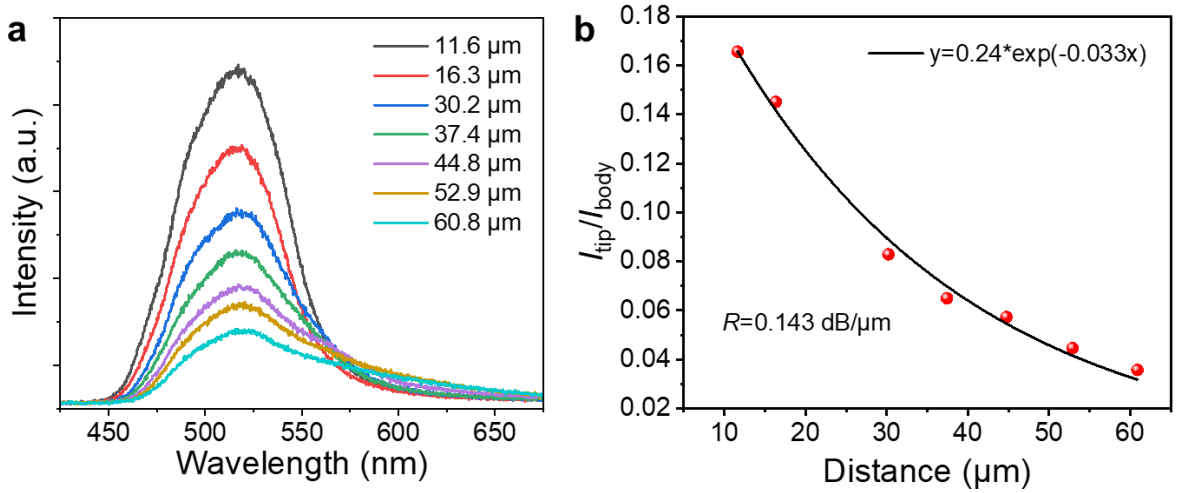


**Figure S11.** a) The spatially resolved PL spectra of Py-TCP and b) their curve of intensity $I_{tip}/I_{body}$ with distance D.

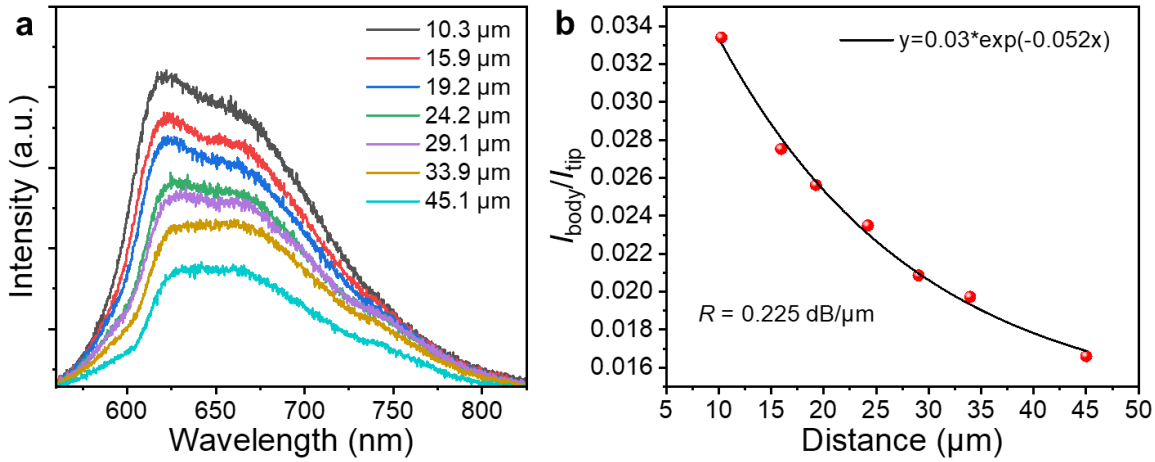


**Figure S12.** a) The spatially resolved PL spectra of Py-OFAQ and b) their curve of intensity $I_{tip}/I_{body}$ with distance D.


**Figure S13.** a) The Pattern of quick response (QR) code and b) the corresponding information obtained by scanning the code.

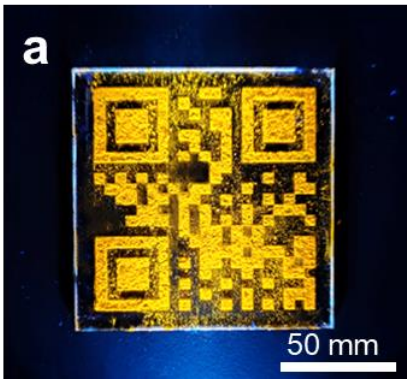


**Figure S14.** a) The prepared QR code with yellow emission made from Py-TCNB.

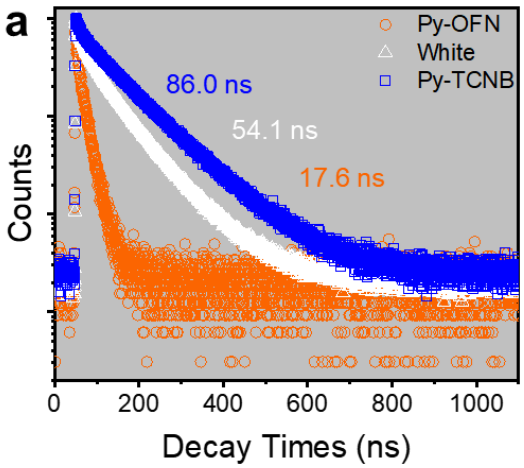


**Figure S15.** a) The time-resolved fluorescence decay spectrum of Py-OFN, Py-TCNB and Py-TCNB$_{0.1}$-OFN$_{0.9}$.

**Table S1.** The CIE coordinates of pyrene-based cocrystals.

| Complexes | X | Y |
|---|---|---|
| Pyrene | 0.1937 | 0.3510 |
| Py-OFN | 0.1653 | 0.1767 |
| Py-TFP | 0.2116 | 0.4019 |
| Py-TCP | 0.2397 | 0.5701 |
| Py-TCNB | 0.4641 | 0.5282 |
| Py-DCAQ | 0.5665 | 0.4313 |
| Py-OFAQ | 0.6379 | 0.3615 |
| Py-DNAQ | 0.7038 | 0.2961 |
| Py-TCNQ | 0.6011 | 0.3981 |
| Py-FTCNQ | 0.6554 | 0.3443 |
| Py-$F_2$TCNQ | 0.6714 | 0.3284 |
| Py-$F_4$TCNQ | 0.7347 | 0.2653 |

**Table S2.** Crystalline parameters of Pyrene, Py-OFN, Py-TCNB, and Py-DNAQ.

| **Compound** | Pyrene | Py-OFN | Py-TCNB | Py-DNAQ |
|---|---|---|---|---|
| **CCDC** | 1240734 | 1977445 | 2026238 | 1847614 |
| **Empirical formula** | $C_{16}H_{10}$ | $C_{16}H_{10}$ $C_{10}F_8$ | $C_{16}H_{10}$ $C_{10}H_2N_4$ | $C_{16}H_{10}$ $C_{14}H_6N_2O_6$ |
| **Formula weight** | 202.25 | 474.35 | 380.41 | 406.43 |
| **Space group** | $P2_1/a(14)$ | $P2_1/c(14)$ | $P2_1/c(14)$ | $Pca2_1(29)$ |
| **Crystal system** | Monoclinic | Monoclinic | Monoclinic | Orthorhombic |
| **a [Å]** | 13.649 | 6.7029(4) | 7.1035(6) | 20.145(16) |
| **b [Å]** | 9.256 | 16.2474(8) | 8.3754(7) | 7.169(6) |
| **c [Å]** | 8.470 | 25.8334(15) | 15.5184(15) | 15.362(12) |
| **α [°]** | 90.00 | 90.00 | 90.00 | 90.00 |
| **β [°]** | 100.28 | 91.907(6) | 93.831(3) | 90.00 |
| **γ [°]** | 90.00 | 90.00 | 90.00 | 90.00 |
| **Volume V [Å3]** | 1052.88 | 2811.82 | 921.199 | 2218.57 |
| **Z, Z' [molecules per cell]** | 4, 1 | 6, 1.5 | 2, 0.5 | 4, 1 |

**Table S3.** Crystalline parameters of Py-TCNQ, Py-FTCNQ, Py-F2TCNQ, Py-F4TCNQ.

| **Compound** | Py-TCNQ | Py-FTCNQ | Py-$F_2$TCNQ | Py-$F_4$TCNQ |
|---|---|---|---|---|
| **CCDC** | 957181 | 2294644 | 2294645 | 1845460 |
| **Empirical formula** | $C_{16}H_{10}$, $C_{12}H_4N_4$ | $C_{16}H_{10}$, $C_{12}H_3FN_4$ | $C_{16}H_{10}$, $C_{12}H_2F_2N_4$ | $C_{16}H_{10}$, $C_{12}F_4N_4$ |
| **Formula weight** | 406.43 | 424.44 | 442.43 | 478.41 |
| **Space group** | P $2_1$/n(14) | P$2_1$/n(14) | P $2_1$/n(14) | P-1(2) |
| **Crystal system** | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| **a [Å]** | 6.992(1) | 8.9030(16) | 15.346(14) | 6.7671(12) |
| **b [Å]** | 10.069(2) | 13.294(2) | 13.701(3) | 8.867(2) |
| **c [Å]** | 14.671(3) | 17.241(3) | 19.229(2) | 9.6974(19) |
| **α [°]** | 90.00 | 90.00 | 90.00 | 102.917(6) |
| **β [°]** | 103.52(3) | 100.531(6) | 99.260(9) | 109.917(6) |
| **γ [°]** | 90.00 | 90.00 | 90.00 | 101.864(6) |
| **Volume V [Å3]** | 1004.2 | 2006.21 | 3990.42 | 507.407 |
| **Z, Z' [molecules per cell]** | 2, 0.5 | 4, 1 | 4, 1 | 1, 0.5 |

## References


1. Gavezzotti A, Filippini G. *J Phys Chem*, **1994**, 98, 4831-4837.
2. Gavezzotti A. *Acc Chem Res*, **1994**, 27, 309-314.
3. Frisch M, Trucks G, Schlegel H, Scuseria G, Robb M, Cheeseman J, Scalmani G, Barone V, Petersson G, Nakatsuji H, Li X, Caricato M, Marenich A, Bloino J, Janesko B, Gomperts R, Mennucci B, Hratchian H, Ortiz J, Izmaylov A, Sonnenberg J, Williams, Ding F, Lipparini F, Egidi F, Goings J, Peng B, Petrone A, Henderson T, Ranasinghe D, Zakrzewski V, Gao J, Rega N, Zheng G, Liang W, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Throssell K, Montgomery Jr. J, Peralta J, Ogliaro F, Bearpark M, Heyd J, Brothers E, Kudin K, Staroverov V, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J, Iyengar S, Tomasi J, Cossi M, Millam J, Klene M, Adamo C, Cammi R, Ochterski J, Martin R, Morokuma K, Farkas O, Foresman J, Fox D. Gaussian 09, Revision E.01, Gaussian Inc., Wallingford, CT, 2016.