Supporting Information: Theobromine and Direct Arylation: A Sustainable and Scalable Solution to Minimize Aggregation Caused Quenching

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Contents

1. Material synthesis

Table S1. Price comparison of starting materials of each synthetic route in **Fig. 1**.

	Starting material	Price	Purchase website
Huang et al.	dibromofluorene	\$173.00/25g	https://www.sigmaaldrich.com/catalog/product/aldrich/342297?lang=en&region=US
Tang et al.	1-bromo-4-(1,2,2-triphenylethenyl)benzene	\$198.00/2g	https://www.sigmaaldrich.com/catalog/product/aldrich/900647?lang=en&region=US
This method	theobromine	\$36.60/25g	https://www.sigmaaldrich.com/catalog/product/sigma/t4500?lang=en&region=US

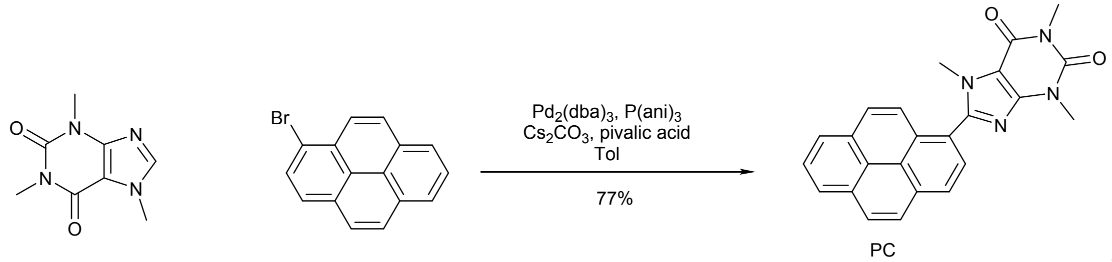
Theobromine, 1-bromooctane, 1-bromopyrene, 1,6-dibromopyrene, 1,3,6,8-tetrabromopyrene and tris(2-methoxyphenyl)phosphine were purchase from TCI. Bis(dibenzylideneacetone)palladium(0) and pivalic acid were purchased from Sigma Aldrich. Solvents used were purified *via* a PureSolv solvent purification system from Inert Inc. K_2CO_3 and Cs_2CO_3 were ground into a powder and dried at 120 ^oC overnight before reactions. Reactions were run under N_2 atmosphere using standard Schlenk techniques and detailed synthesis procedures are described below.

3,7-dimethyl-1-octyl-3,7-dihydro-1H-purine-2,6-dione (Theo8). Into a 500 mL round bottom flask, theobromine (18.0 g, 100 mmol), 1-bromooctane (23.2 g, 120 mmol), dried K_2CO_3 (20.7 g, 150 mmol) and 200 mL DMF was added. The system was degassed and then heated to 120 ^oC overnight. When finished, the reaction was cooled to room temperature. ethyl acetate was used to extract the product and brine was used to remove residue DMF. The organic layer was subsequently washed with brine to remove the DMF in the organic phase. The organic layer was then dried over Mg_2SO_4 and concentrated under reduced pressure. The crude product was further purified with column chromatography using dichloromethane/methanol in a 10:1 ratio as an eluent. The collected fraction was then recrystallized from hexane. 25.7 g of collected white solid was collected, with 96% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 4.02 – 3.97 (m, 5H), 3.57 (s, 3H), 1.70 – 1.58 (m, 2H), 1.47 – 1.20 (m, 10H), 0.92 – 0.82 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.17, 151.41, 148.73, 141.61, 107.59, 41.39, 33.48, 31.84, 29.56, 29.34, 29.24, 28.12, 27.05, 22.64, 14.07.

3,7-dimethyl-1-octyl-8-(pyren-1-yl)-3,7-dihydro-1H-purine-2,6-dione (PT1). Theo8 (552 mg, 2 mmol) and 1-bromopyrene (562 mg, 2 mmol), pivalic acid (40 mg, 0.4 mmol) and dried Cs_2CO_3 (1.30 g, 4 mmol) were added into a 25 mL round bottom flask. 10 ml toluene was then adding into the system followed by degassing with N_2 flow for 10 min. Tris(2-methoxyphenyl)phosphine (56 mg , 0.097 mmol) and bis(dibenzylideneacetone)palladium(0) (40 mg, 0.044 mmol) were added to the solution under N_2 flow, and the solution turned purple. The flask was then sealed with a rubber stopper and heated to 100 ^oC. After reacting for 1 day, the system was cooled and filtered. The organic phase was then concentrated under reduced pressure. The crude product was further purified with column chromatography using chloroform/methanol in a 400:5 ratio as an eluent (chloroform/methanol = 400/5). 715 mg of white solid was obtained in a 75% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 2.5 Hz, 1H), 8.28 (d, *J* = 2.5 Hz, 1H), 8.26 (d, *J* = 10 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 8.15 (q, 2H), 8.08 (t, 2H), 7.92 (d, *J* = 9.2 Hz, 1H), 4.19 – 4.02 (m, 2H), 3.83 (s, 3H), 3.70 (s, 3H), 1.83 – 1.69 (m, 2H), 1.50 – 1.23 (m, 10H), 0.98 – 0.83 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.58, 152.03, 151.65, 150.16, 148.59, 132.90, 131.26, 130.74, 130.40, 129.40, 129.14, 127.80, 127.19, 126.61, 126.30, 126.08, 124.84, 124.60, 124.42, 123.90, 122.40, 108.58, 41.67, 33.49, 31.88, 29.88, 29.29, 28.27, 27.14, 22.67, 14.08.

8,8'-(pyrene-1,6-diyl)bis(3,7-dimethyl-1-octyl-3,7-dihydro-1H-purine-2,6-dione) (PT2). Theo8 (1,932 mg, 7 mmol) and 1,6-dibromopyrene (1,080 mg, 3 mmol), pivalic acid (80 mg, 0.8 mmol) and dried Cs_2CO_3 (3 g, 9 mmol) were added into a 50 mL round bottom flask. 25 mL toluene was then adding into the flask, followed by degassing with N_2 flow for 10 min. Tris(2-methoxyphenyl)phosphine (122 mg, 0.194 mmol) and bis(dibenzylideneacetone)palladium(0) (80 mg, 0.088 mmol) were added to the solution under N_2 flow, and the solution turned purple. The flask was then sealed with a rubber stopper and heated to 100 °C. After reacting for 1 day, the system was cooled and filtered. The organic phase was then concentrated under reduced pressure. The crude product was further purified with column chromatography using chloroform/methanol in a ratio of 400/5 as an eluent. 1,472 mg pale yellow solid was obtained in a 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.9 Hz, 2H), 8.23 (d, *J* = 9.2 Hz, 2H), 8.16 (d, *J* = 7.9 Hz, 2H), 8.09 (d, *J* = 9.2 Hz, 2H), 4.16 – 4.05 (m, 4H), 3.88 (s, 6H), 3.71 (s, 6H), 1.80 – 1.69 (m, 2H), 1.51 – 1.22 (m, 20H), 0.94 – 0.85 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.54, 151.55, 151.38, 148.51, 132.31, 130.48, 129.11, 128.51, 125.64, 124.54, 123.65, 108.66, 41.68, 33.59, 31.86, 29.89, 29.39, 29.27, 28.23, 27.11, 22.66, 14.11.

8,8',8'',8'''-(pyrene-1,3,6,8-tetrayl)tetrakis(3,7-dimethyl-1-octyl-3,7-dihydro-1H-purine-2,6-dione) (PT4). **Theo8** (1,932 mg, 76 mmol) and 1,3,6,8-tetrabromopyrene (517 mg, 1 mmol), pivalic acid (80 mg, 0.8 mmol) and dried Cs_2CO_3 (3 g, 9 mmol) were added into a 50 mL round bottom flask. 15 mL toluene was then adding into the system followed by degassing with N_2 flow for 10 min. Tris(2-methoxyphenyl)phosphine (122 mg , 0.194 mmol) and bis(dibenzylideneacetone)palladium(0) (80 mg, 0.088 mmol) were added to the solution under N_2 flow, and the solution turned purple. The flask was then sealed with a rubber stopper and heated to 100 °C. After reacting for 1 day, the system was cooled and filtered. The organic phase was then concentrated under reduced pressure. The crude product was purified with column chromatography using chloroform/methanol in a ratio of 40:1 as an eluent. 585 mg green-yellow solid was obtained in a 43% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 2H), 8.27 (s, 4H), 4.08 (t, 8H), 3.91 (s, 12H), 3.68 (s, 12H), 1.73 (m, 8H), 1.47 – 1.23 (m, 40H), 0.92 – 0.87 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.44, 151.42, 149.53, 148.51, 131.43, 131.14, 127.32, 124.79, 124.64, 109.01, 41.76, 33.86, 31.84, 29.89, 29.37, 29.26, 28.18, 27.08, 22.66, 14.10.



Scheme S1. Synthesis of PC from caffeine and 1-bromopyrene via direct arylation.

1,3,7-trimethyl -8-(pyren-1-yl)-3,7-dihydro-1H-purine-2,6-dione (PC). Caffeine (388 mg, 2 mmol) and 1-bromopyrene (562 mg, 2 mmol), pivalic acid (40 mg, 0.4 mmol) and dried Cs_2CO_3 (1.30 g, 4 mmol) were added into a 25 mL round bottom flask. 10 ml toluene was then adding into the system followed by degassing with N_2 flow for 10 min. Tris(2-methoxyphenyl)phosphine (56 mg , 0.097 mmol) and bis(dibenzylideneacetone)palladium(0) (40 mg, 0.044 mmol) were added to the solution under N_2 flow, and the solution turned purple. The flask was then sealed with a rubber stopper and heated to 100 °C. After reacting for 1 day, the system was cooled and filtered. The organic phase was then concentrated under reduced pressure. The crude product was further purified with column chromatography using chloroform/methanol in a 400:5 ratio as an eluent (chloroform/methanol = 400/5). 605 mg of white solid was obtained in a 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, J = 1.7 Hz, 1H), 8.28 (d, J = 1.4 Hz, 1H), 8.26 – 8.22 (m, 1H), 8.19 (d, J = 4.6 Hz, 1H), 8.15 (d, J = 2.2 Hz, 1H), 8.12 (d, J = 4.6 Hz, 1H), 8.09 (d, J = 2.2 Hz, 1H), 8.06 (d, J = 1.9 Hz, 1H), 7.91 (d, J = 9.2 Hz, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13C NMR (75 MHz, CDCl3) δ 155.75, 151.98, 148.40, 145.98, 132.93, 131.20, 130.67, 130.25, 129.39, 129.13, 127.76, 127.15, 126.58, 126.28, 126.05, 124.57, 123.79, 122.11, 108.38, 33.47, 29.91, 28.02.

2. UV-vis and PL spectra in solution and as thin film

Absorption spectra of chemicals were obtained using a Perkin Elmer Lambda 950 – UV Vis/NIR spectrophotometer while the photoluminescence spectrums were obtained using a homemade instrument. Solution samples were prepared by dissolving **PT1**, **PT2** and **PT4** in to chloroform with concentration of 10^{-5} M. Thin film samples were prepared by spincoating 10 mg/mL chloroform solutions of **PT1**, **PT2** and **PT4** respectively onto glass substrates in rate of 1000 rpm.

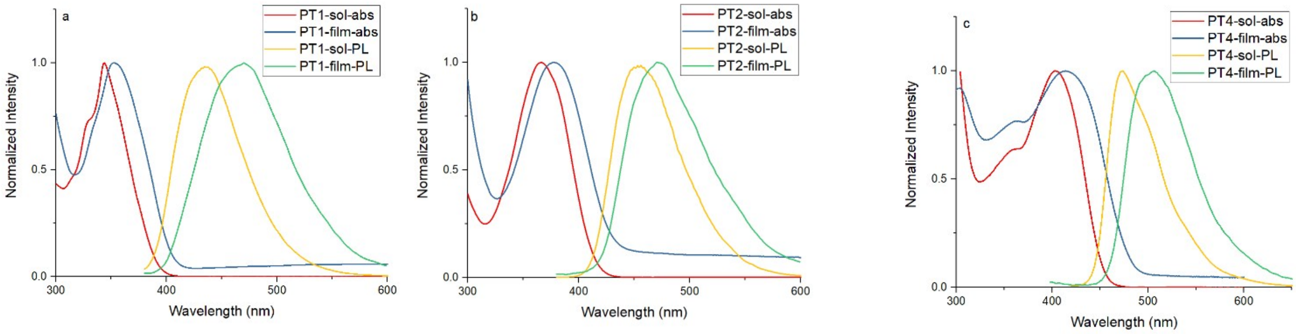


Fig. S1. Absorption and PL spectra of a) **PT1**, b) **PT2** and c) **PT4** in the concentration of 10^{-5} M at room temperature.

3. Density function theory

Chemical structures of all three molecules were imported from Chemdraw into Gaussview 5.0. Density functional theory calculations were performed using the Gaussian 09 software package. Structure optimizations were performed under the B3LYP functional and 6-31g (d) basis set. Once the optimization was complete and the structure was checked for imaginary frequencies, the saved checkpoint files were converted to cube files using the cubegen utility. The cube files were opened in Gaussview 5.0 so that images of the molecular orbitals of each molecule could be taken. This work was facilitated though the use of advanced computational, storage, and networking infrastructure provided by the Hyak supercomputer system and funded by the STF at the University of Washington.

4. Solvatochromic experiments

Absorption spectra were obtained using a Perkin Elmer Lambda 950 – UV Vis/NIR spectrophotometer while the photoluminescence spectrums were obtained using a homemade instrument. Solution samples were prepared by dissolving **PT1**, **PT2** and **PT4** into solvents with concentration of 10^{-5} M.

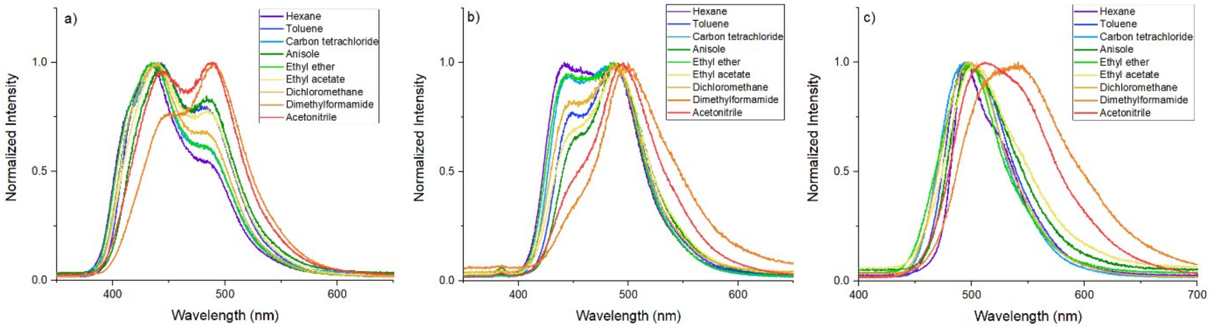


Fig. S2. PL solvatochromic experiments of a) **PT1**, b) **PT2** and c) **PT4** in the concentration of 10^{-5} M at room temperature.

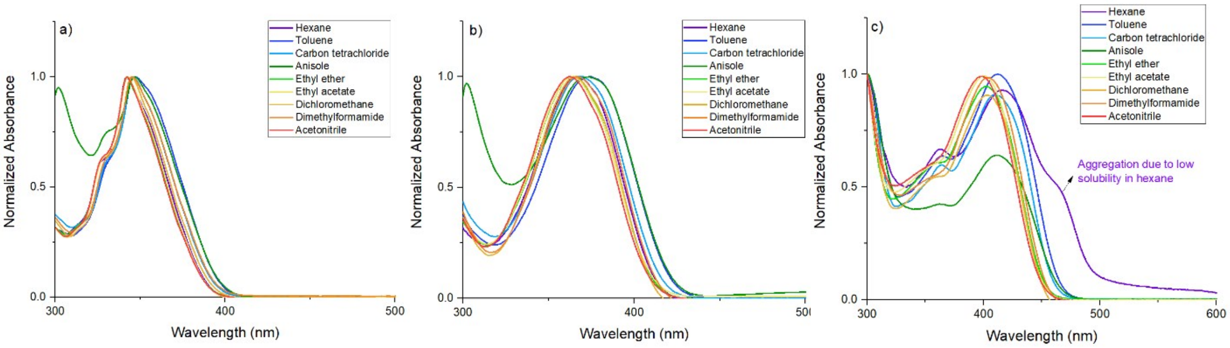


Fig. S3. Absorption solvatochromic experiments of a) **PT1**, b) **PT2** and c) **PT4** in the concentration of 10^{-5} M at room temperature.

of ICT states, they are stabilized by the polar environment and thus their energy levels downshift as solvent polarity increases, as illustrated in **Fig. S4**. On the other hand, the energy level of LE state changes little with solvent polarity. Because **PT1**, **PT2** and **PT4** possess LE states and ICT states that are energetically adjacent, one can tune the crossover of their contributions to the HLCT state – in this case from LE state dominant to ICT state don fting the ICT state energy.

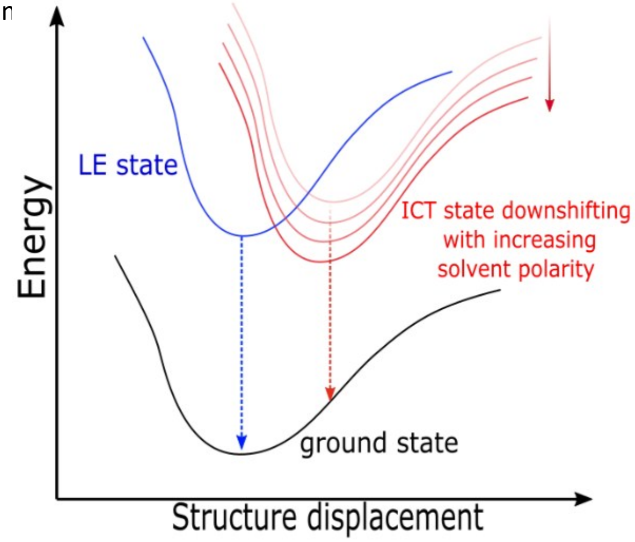


Fig. S4. Energy level shifts of LE states and ICT states as the change of solvent polarity.

5. Amplified spontaneous emission measurement and simulation

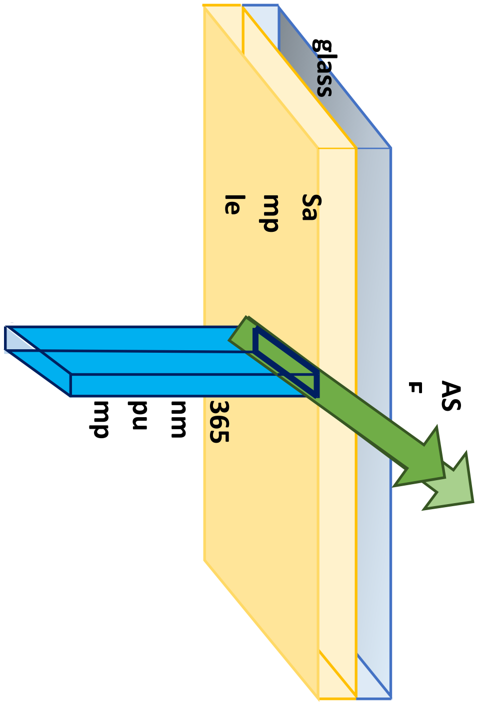


Fig. S5. Setup of ASE measurement.

To measure the ASE, we spincoated PT solution on a glass substrate to form an optical waveguide with SiO2 and air on each side. A 375 nm laser beam was focused through a cylindrical lens to achieve a radiation area of 0.8mm x 2mm and photoexcite the film at a normal angle (**Fig. S5**). One end of the photoexcitation stripe was aligned to be flush to the edge of the film to minimize loss. Photoluminescence from the edge of the film was collected at various photopump intensities. The measurements were performed under dynamic vacuum by placing the film in a custom-made vacuum chamber to prevent film degradation.

Pump mode overlap (PMO) is and mode confinement (MC) was calculated using equations below:

$$PMO = \frac{\int_0^d E_{pump} E_{mode}(z) dz}{\int_0^d E_{mode}(z) dz}$$

$$MC = \frac{\int_0^d E_{mode}(z) dz}{\int_{-\infty}^{+\infty} E_{mode}(z) dz}$$

E_{pump} was calculated using a previously reported transfer matrix method. $E_{mode}(z)$ was determined via simulation of the waveguiding of the 0-1 emission in a SiO_2-PT film-air slab using the FEEM solver in Lumerical DEVICE. Optical constants used in the simulation and calculation were determined by globally fitting various angle spectroscopic ellipsometric (VASE) to a B-Spline model. Specifically, data at transparent wavelengths were first fitted to a Cauchy model. We then extended the fitting region to the absorbing region using a B-spline model.

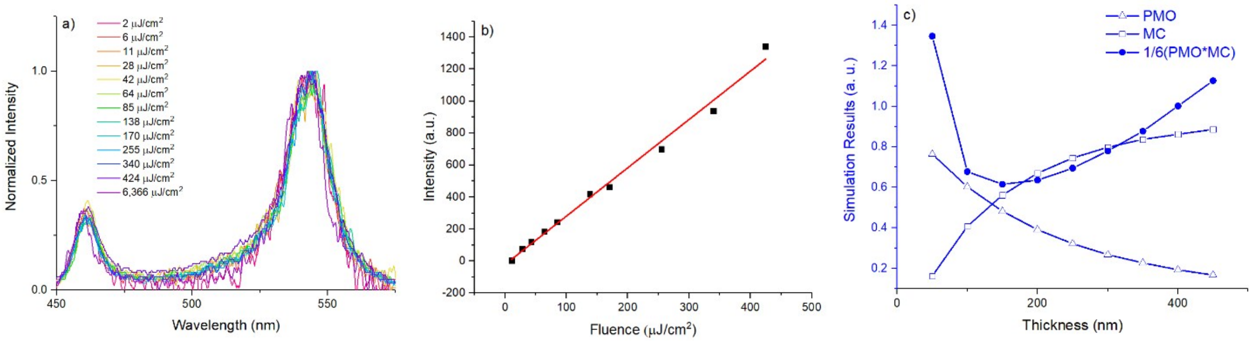


Fig. S6. a) Emission spectra of a ~50 nm thick **PT1** film collected from the edge with different excitation. b) Output intensity from the film edge as a function of the excitation fluence. c) PMO and MC modelling of **PT1** and PMO*MC was scaled to fit in the same plot.

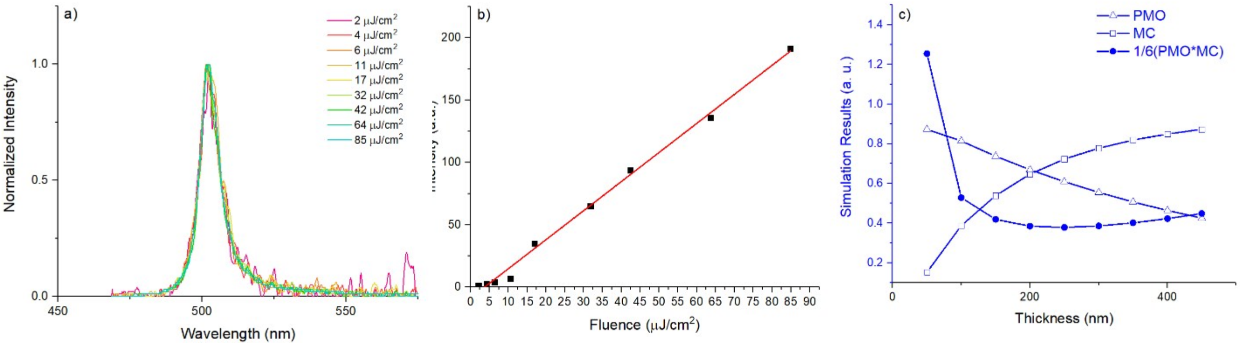


Fig. S7. a) Emission spectra of a ~50 nm thick **PT4** film collected from the edge with different excitation. b) Output intensity from the film edge as a function of the excitation fluence. c) PMO and MC modelling of **PT4** and PMO*MC was scaled to fit in the same plot.

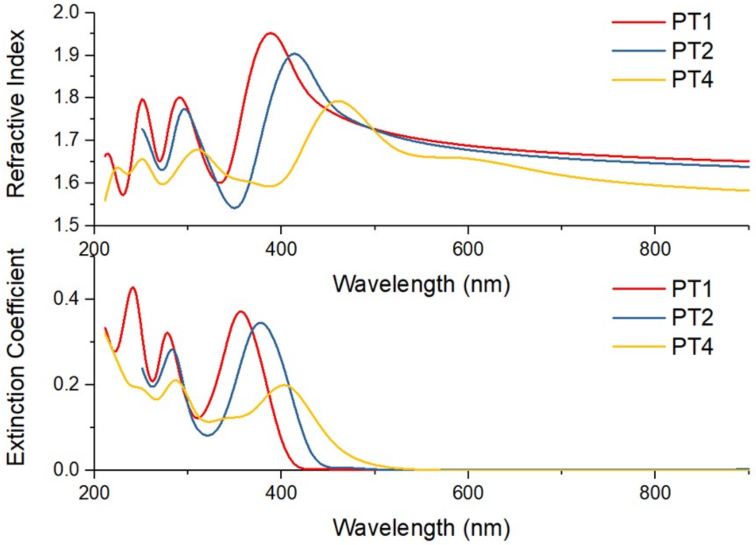


Fig. S8. Refractive index and extinction coefficient used for ASE threshold simulation.

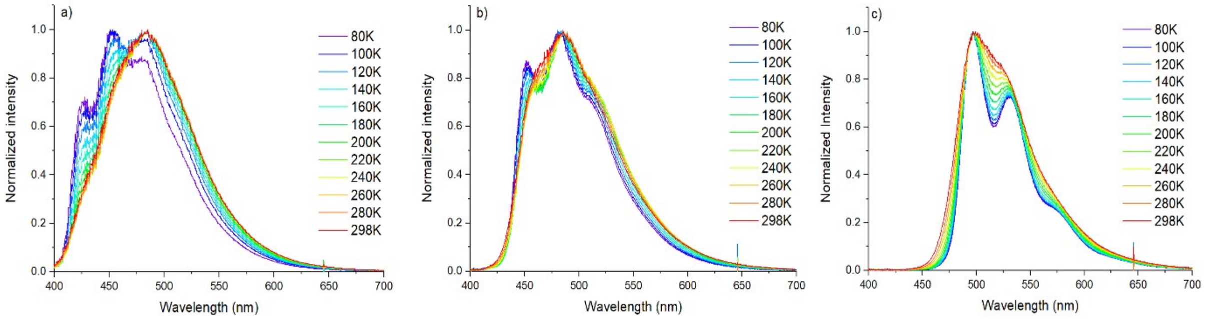
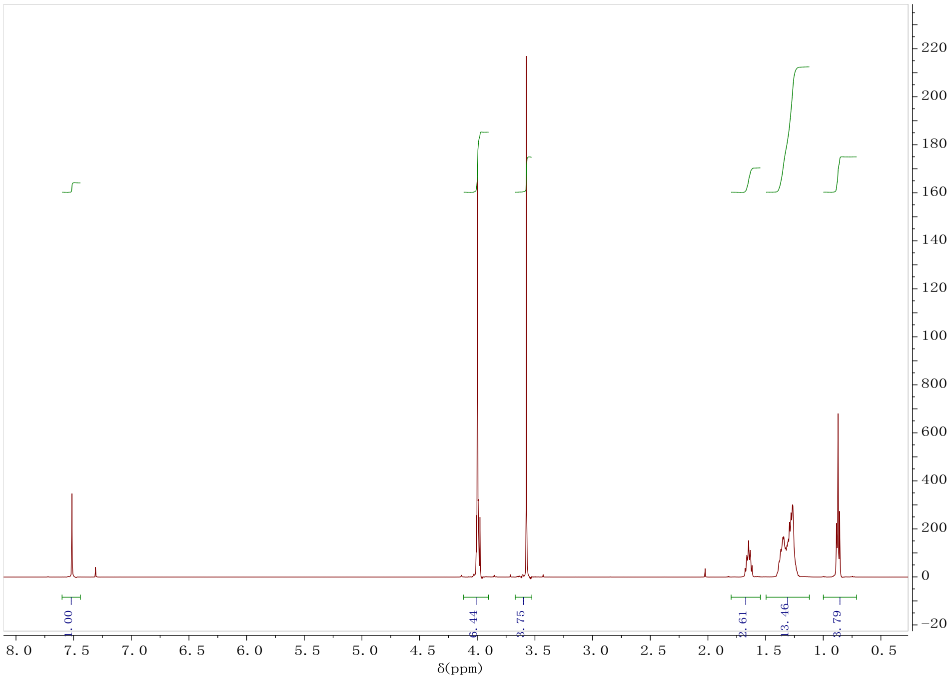


Fig. S9. Temperature dependent PL spectra of a) **PT1**, b) **PT2** and c) **PT4** in chloroform solution with the concentration of 10^{-5} M.

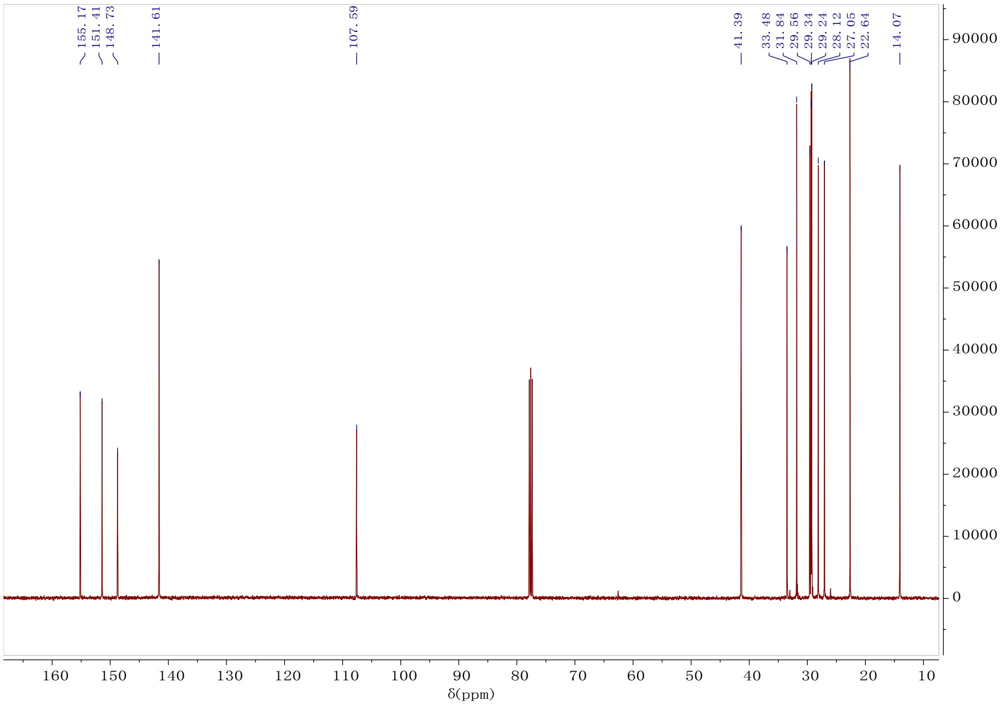
6. NMR spectra

Theo8

^{1}H NMR (500 MHz, Chloroform-*d*)

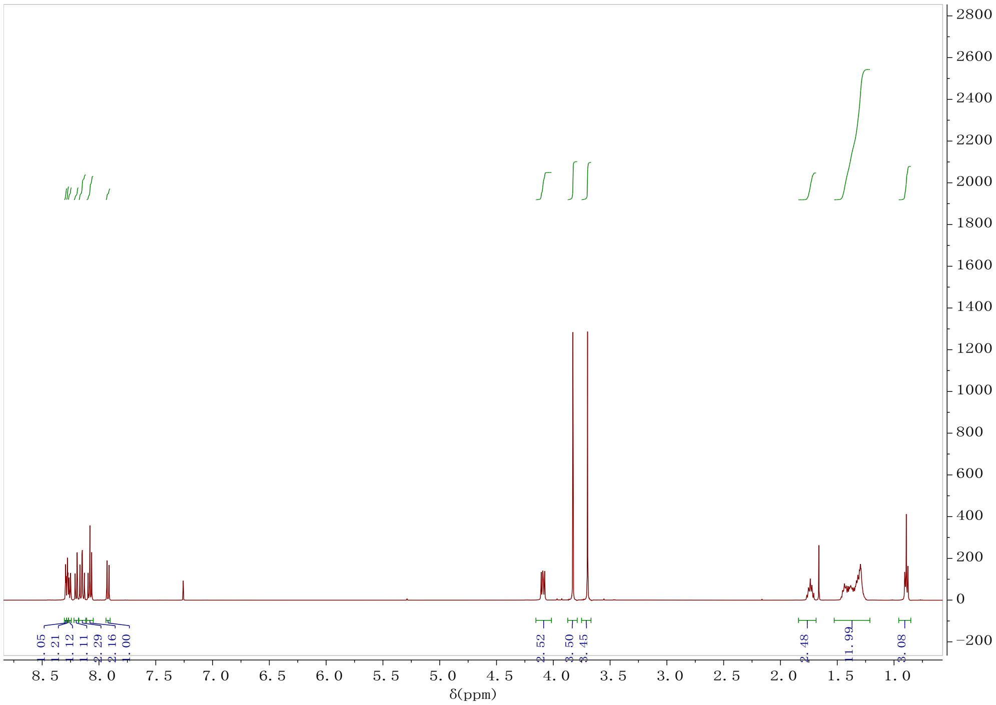


^{13}C NMR (126 MHz, CDCl$_3$)

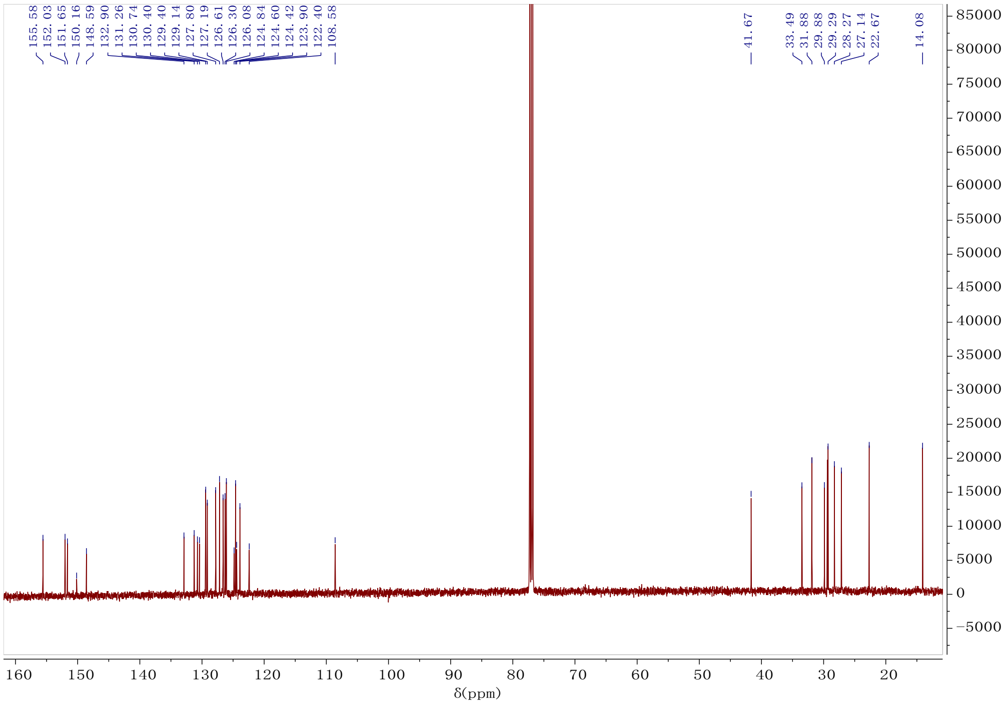


PT1

^{1}H NMR (500 MHz, Chloroform-*d*)

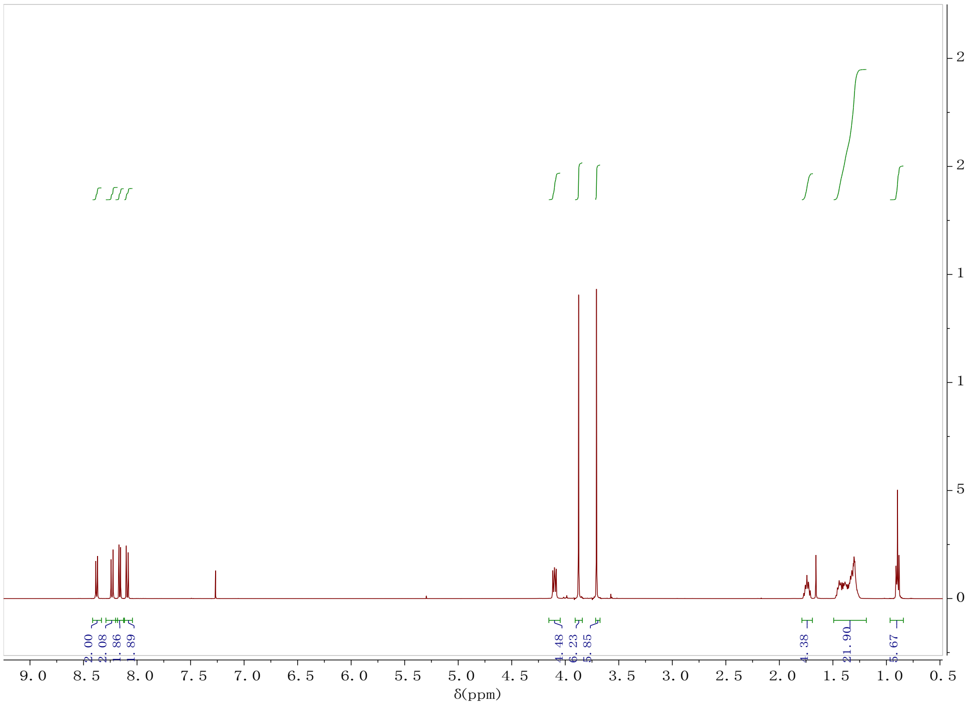


^{13}C NMR (126 MHz, CDCl$_3$)

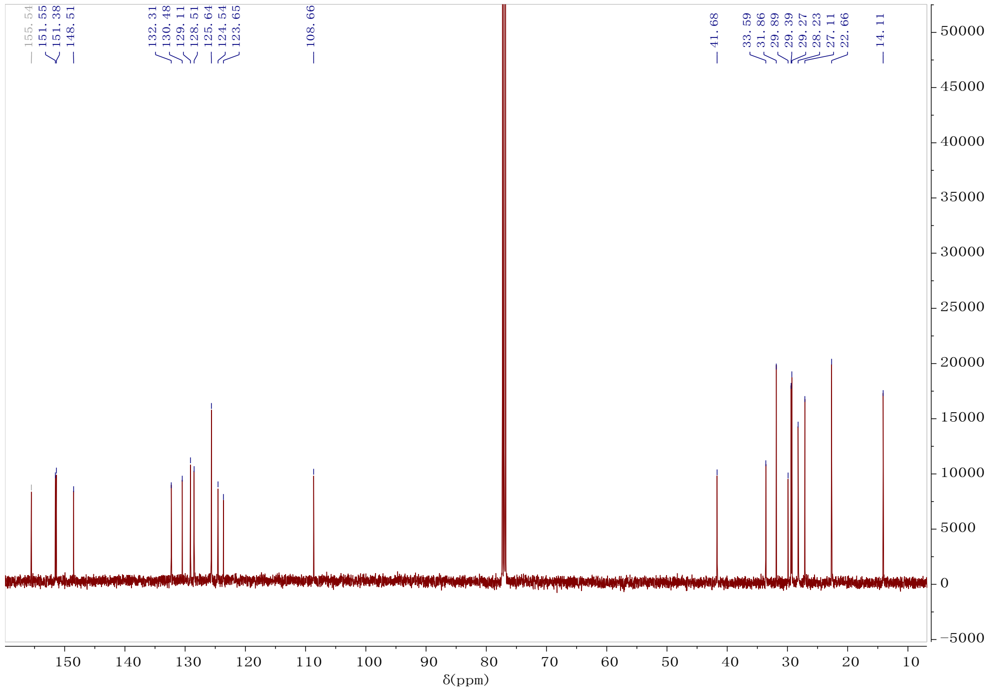


PT2

^{1}H NMR (500 MHz, Chloroform-*d*)

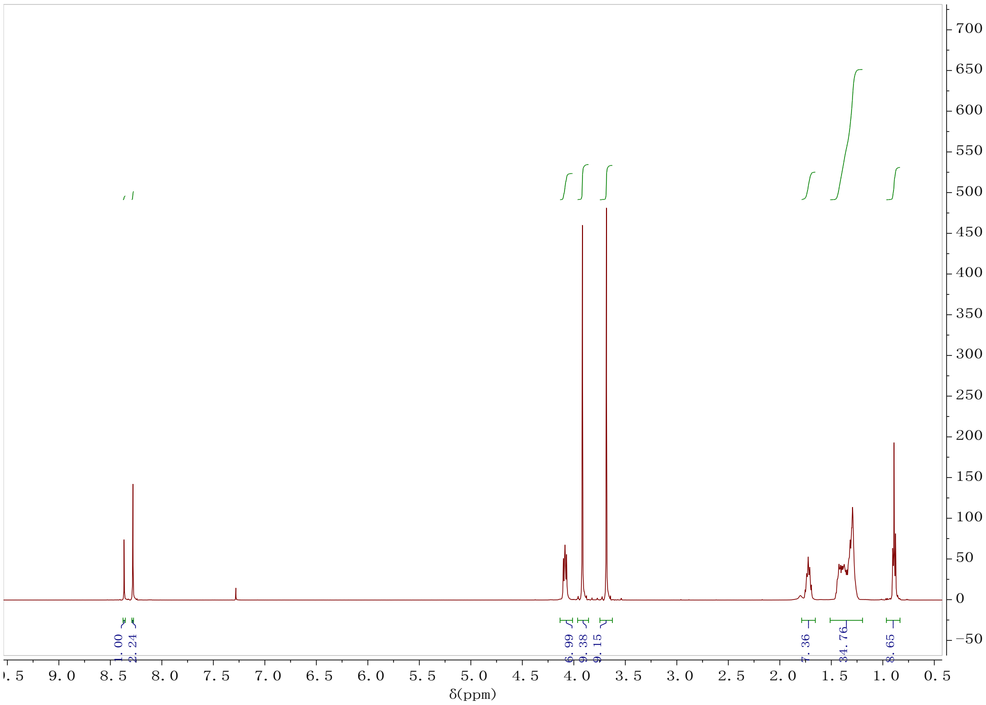


^{13}C NMR (126 MHz, CDCl$_3$)

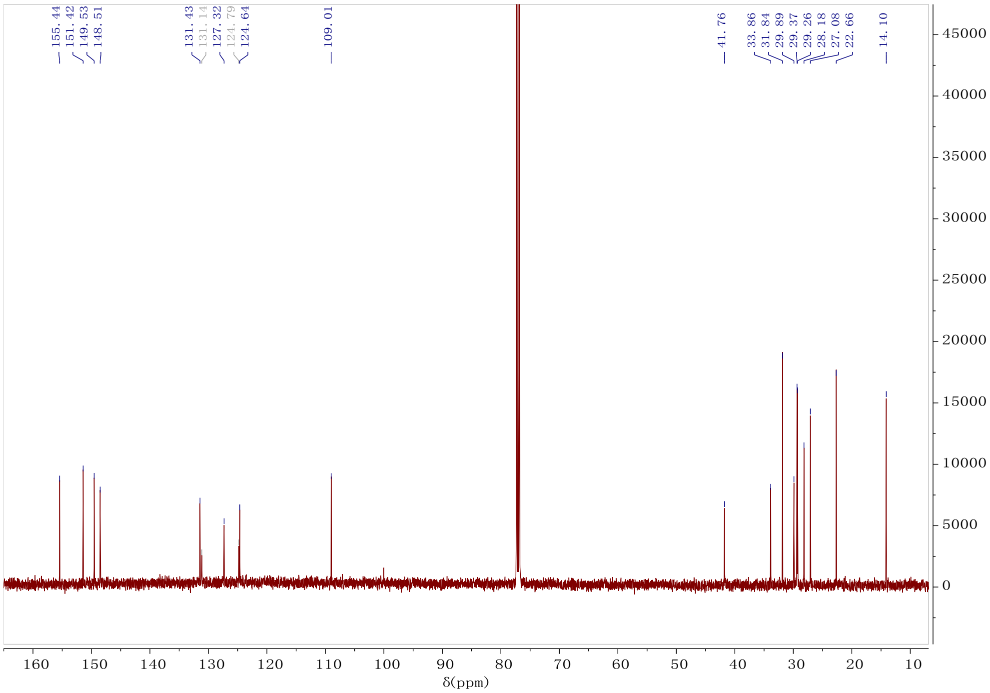


PT4

^{1}H NMR (500 MHz, Chloroform-*d*)

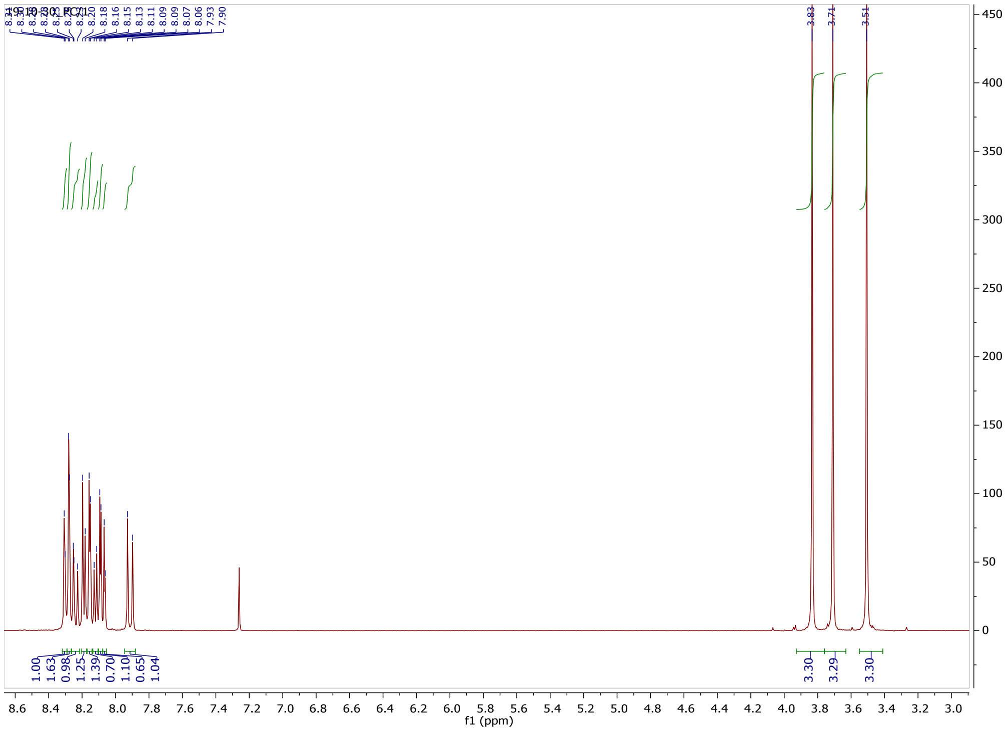


^{13}C NMR (126 MHz, CDCl$_3$)

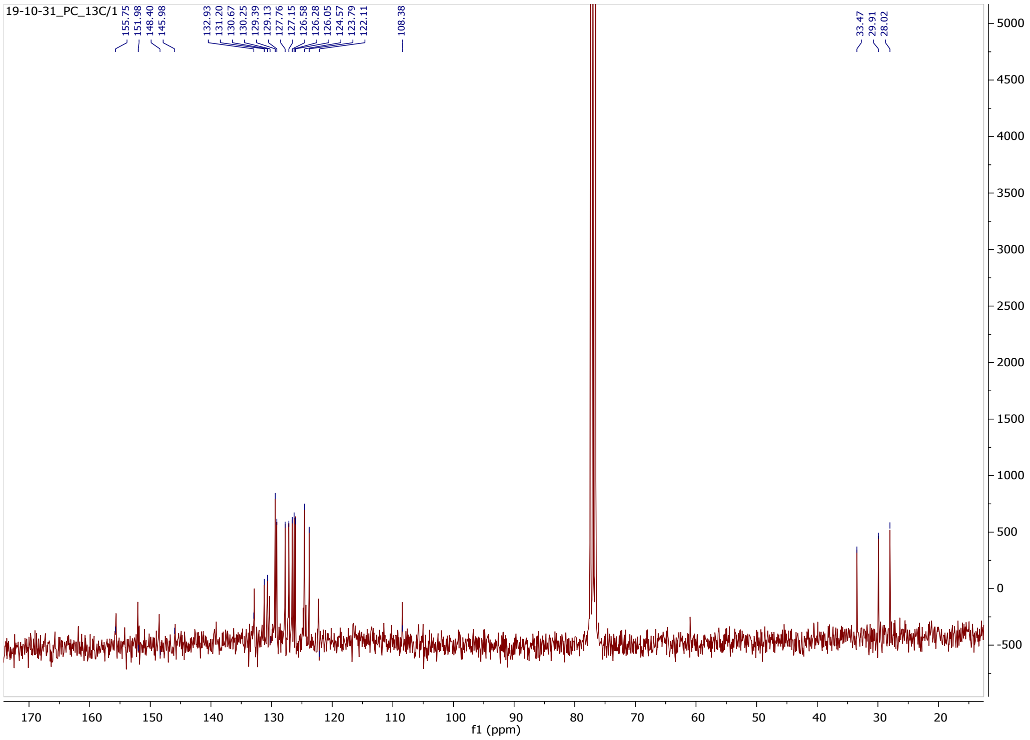


PC

^{1}H NMR (300 MHz, Chloroform-*d*)



^{13}C NMR (75 MHz, CDCl$_3$)



7. X-Ray Structures

A colorless prism for PT1, measuring 0.60 x 0.17 x 0.04 mm^3, a pale green plate (PT2) measuring 0.16 x 0.04 x 0.01 mm^3, and a yellow prism for PT4, measuring 0.34 x 0.09 x 0.07 mm^3 were mounted on loops with Paratone oil. Data were collected at -173^{o}C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation.

Crystal-to-detector distance was 40 mm and exposure time was 10 seconds (PT1, PT4) and 240 seconds (PT2) per frame for all sets. The scan width was 0.5^{o}. Further data collection details are summarized in Table S1.

The data were integrated and scaled using SAINT, SADABS within the APEX2 software package by Bruker.[1]

Solution by direct methods (SHELXS, SIR97)[2] produced complete heavy atom phasing models consistent with the proposed structure. The structures were completed by difference Fourier synthesis with SHELX.[3,4] Scattering factors are from Waasmair and Kirfel[5]. Hydrogen atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with C---H distances in the range 0.95-1.00 Angstrom. Isotropic thermal parameters Ueq were fixed such that they were 1.2Ueq of their parent atom Ueq for CH's and 1.5Ueq of their parent atom Ueq in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

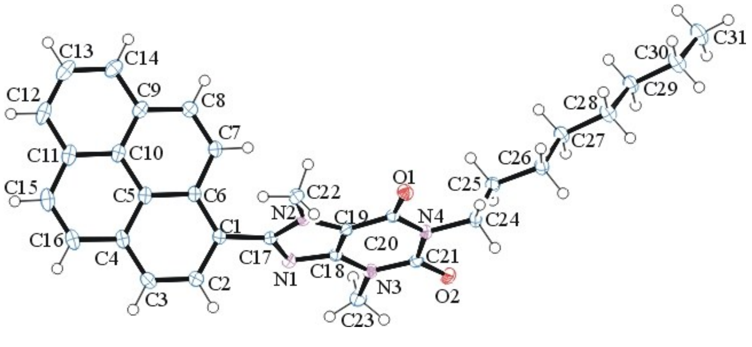


Fig. S10 ORTEP[6] of the structure of PT1 with thermal ellipsoids at the 50% probability level.

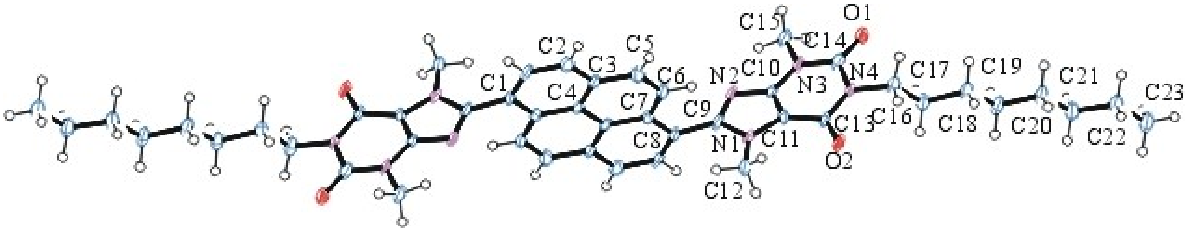


Fig. S11. ORTEP of the structure of PT2 with thermal ellipsoids at the 50% probability level. The content of the asymmetric unit is enumerated, the other half of the molecule is generated through inversion.

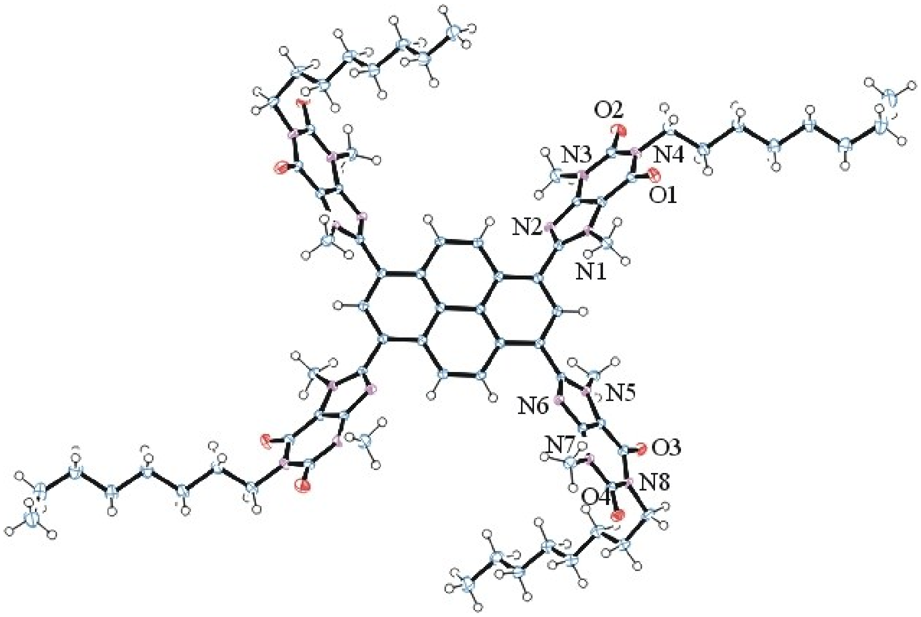


Fig. S12. ORTEP of the structure of PT4 with thermal ellipsoids at the 50% probability level. The content of the asymmetric unit (except carbon atoms) is enumerated, the other half of the molecule is generated through inversion.

TABLE S1

Compound	PT1	PT2	PT4
Empirical formula	C31 H32 N4 O2	C46 H54 N8 O4	C76 H98 N16 O8
Formula weight	492.60	782.97	1363.70
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P 2_1/c	P $\bar{1}$	P 2_1/c
Unit cell dimensions	a = 21.6000(16) Å	a = 4.7211(18) Å	a = 11.4759(7) Å
	b = 12.9539(10) Å	b = 13.737(5) Å	b = 23.1694(15) Å
	c = 8.9450(6) Å	c = 15.384(6) Å	c = 14.5016(10) Å
	α= 90°	α= 77.216(14)°	α= 90°

	β= 90.508(4)°	β= 86.717(15)°	β= 111.004(3)°
	γ = 90°	γ = 85.596(18)°	γ = 90°
Volume	2502.8(3) Å^3	969.3(6) Å^3	3599.6(4) Å^3
Z	4	1	2
Density (calculated)	1.307 Mg/m^3	1.341 Mg/m^3	1.258 Mg/m^3
Absorption coefficient	0.083 mm^{-1}	0.088 mm^{-1}	0.084 mm^{-1}
F(000)	1048	418	1460
Crystal size (mm^3)	0.600 x 0.170 x 0.040	0.160 x 0.040 x 0.010	0.340 x 0.090 x 0.070
Theta range	1.833 to 28.343°.	1.523 to 25.155°.	1.742 to 28.352°.
Index ranges h, k, l	±28, ±17, ±11	±5, ±14, ±18	±15, ±30, ±19
Reflections collected	12181	4805	17739
Independent reflections	6225 [R(int) = 0.0289]	3404 [R(int) = 0.1113]	8986 [R(int) = 0.0347]
Completeness to θ=25°	99.9 %	97.5 %	100.0 %
Data / restr. / param.	6225 / 0 / 338	3404 / 162 / 265	8986 / 0 / 457
Goodness-of-fit on F^2	1.020	0.915	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1041	R1 = 0.0753, wR2 = 0.1400	R1 = 0.0451, wR2 = 0.1040
R indices (all data)	R1 = 0.0687, wR2 = 0.1184	R1 = 0.2578, wR2 = 0.1999	R1 = 0.0784, wR2 = 0.1212

8. Fluorescence image and PLQY lifetime

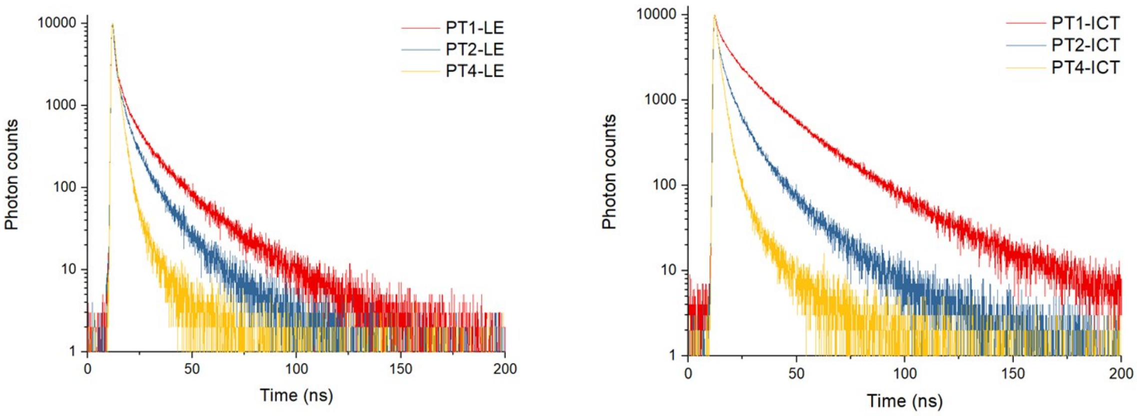


Fig. S13. PLQY lifetime measurements of **PT1, PT2** and **PT4** as thin film.

Table S2. PLQY lifetime values of **PT1**, **PT2** and **PT4** as thin film.

	PT1	**PT2**	**PT4**
LE state lifetime	2.75 ns	1.67 ns	1.78 ns
ICT state lifetime	10.27 ns	2.81 ns	2.15 ns

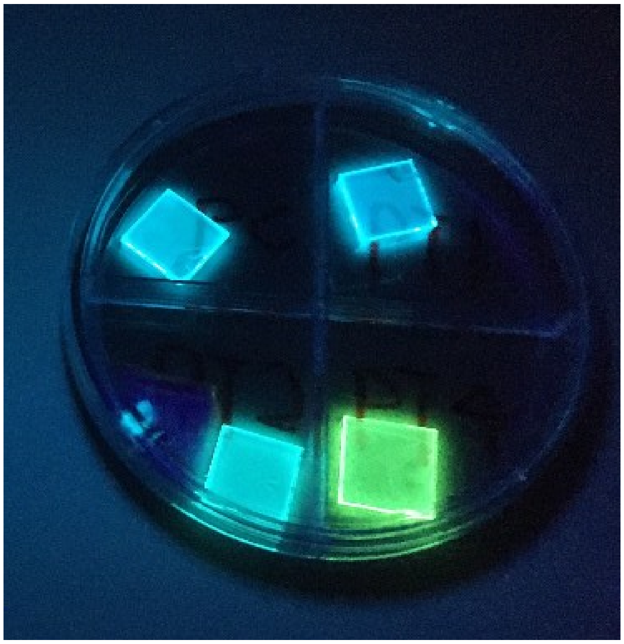


Fig. S14. Newly spincoated films from **PT1**, **PT2** and **PT4** which have been stored in ambience for over 1 year and **PC** that is recently synthesized. (up, left) **PC**, (up, right) **PT1**, (down, left) **PT2**, (down, right) **PT4**.

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