

Supporting Information

A Key Stacking Factor for Effective Formation of Pyrene Excimer in Crystal: Degree of π - π Overlap

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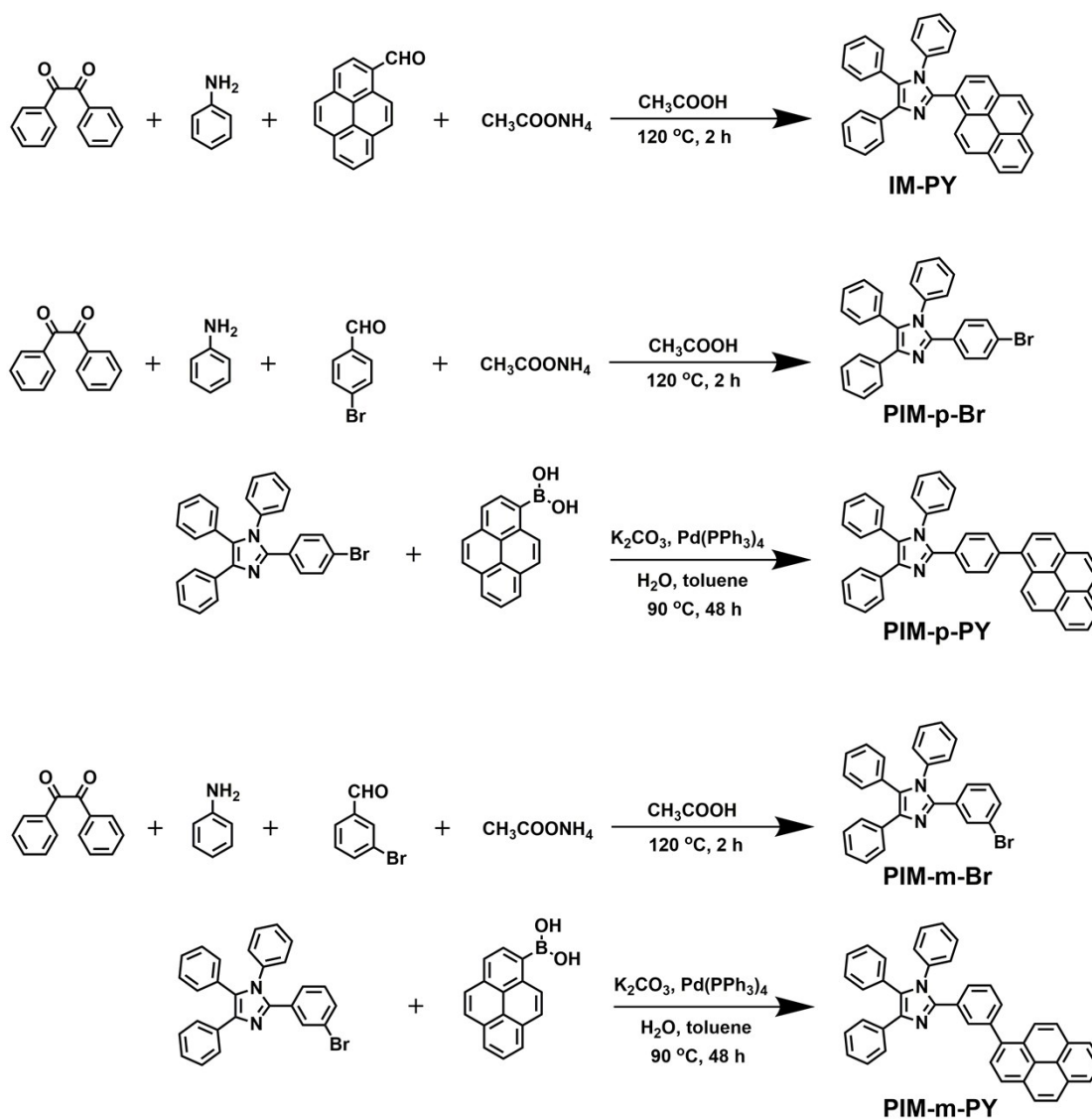
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SI Synthetic details

All the reagents and solvents used for the synthesis were purchased from Aldrich or Acros and used as received. All reactions were performed under nitrogen atmosphere.



Scheme S1. Synthetic routes to IM-PY, PIM-p-PY and PIM-m-PY.

1,4,5-triphenyl-2-(pyren-1-yl)-1H-imidazole (IM-PY)

A mixture of pyrene-1-carbaldehyde (2.30 g, 10.0 mmol), benzil (2.10 g, 10.0 mmol), aniline (3.65 ml, 40.0 mmol), ammonium acetate (3.85 g, 50.0 mmol) and 30 ml acetic acid was refluxed under nitrogen at $120\text{ }^\circ\text{C}$ for 2 h. After the mixture was

cooled down and filtered, the solid product was washed with a 50 mL acetic acid/water mixture (1:1) and 50 mL water, dissolved in CH₂Cl₂ and dried with anhydrous sodium sulfate. It was then purified by chromatography using the mixture of CH₂Cl₂/petroleum ether as an eluent and pure dry product is obtained (2.59 g, yield: 52%). ¹H NMR (500 MHz, DMSO-d₆, 25 °C, TMS): δ = 8.44 (d, *J* = 9.2 Hz, 1H), 8.35 (t, *J* = 7.1 Hz, 2H), 8.27 – 8.22 (m, 2H), 8.21 – 8.15 (m, 2H), 8.12 (t, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.37 (p, *J* = 4.6, 3.9 Hz, 5H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.06 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃, 25 °C, TMS) δ = 146.665 (C), 138.388 (C), 136.713 (C), 134.674 (C), 131.671 (C), 131.220 (C), 131.153 (CH), 130.926 (C), 130.164 (C), 128.735 (CH), 128.675 (CH), 128.534 (CH), 128.261 (CH), 128.197 (CH), 128.053 (CH), 127.990 (CH), 127.731 (CH), 127.609 (CH), 127.300 (CH), 126.716 (CH), 126.126 (CH), 125.542 (CH), 125.457 (CH), 124.823 (C), 124.502 (C), 124.034 (CH). MALDI-TOF MS (mass *m/z*): 496.19 [M⁺]. Anal. calcd (%) for C₃₇H₂₆N₂: C 89.13, H 5.26, N 5.62; found (%): C 89.42, H 5.37, N 5.60.

2-(4-bromophenyl)-1,4,5-triphenyl-1H-imidazole (PIM-p-Br).

A mixture of benzil (2.10 g, 10.0 mmol), 4-bromobenzaldehyde (1.85 g, 10.0 mmol), aniline (3.65 ml, 40.0 mmol), ammonium acetate (3.85 g, 50.0 mmol) and acetic acid (50 mL) was refluxed under nitrogen at 120 °C oil bath for 2 h. After the mixture was cooled down and filtered, the solid product was washed with a 50 mL acetic acid/water mixture (1:1) and 50 mL water, dissolved in CH₂Cl₂ and dried with anhydrous sodium sulfate. It was then purified by silica gel chromatography using the mixture of CH₂Cl₂/petroleum ether as an eluent and pure dry white product is obtained (3.83 g, yield: 85%). ¹H NMR (500 MHz, DMSO-d₆, 25 °C, TMS): δ = 7.54 – 7.46 (m, 4H), 7.39 – 7.33 (m, 3H), 7.31 (dt, *J* = 6.3, 2.5 Hz, 5H), 7.30 – 7.26 (m, 3H), 7.26 – 7.23 (m, 3H), 7.21 – 7.16 (m, 1H). MALDI-TOF MS (mass *m/z*): 450.76 [M⁺].

1,4,5-triphenyl-2-(4-(pyren-1-yl)phenyl)-1H-imidazole (PIM-p-PY)

A mixture of PIM-p-Br (2.03 g, 4.5 mmol), 1-pyrenylboronic acid (1.33 g, 5.4 mmol), K_2CO_3 (6.62 g, 48.0 mmol), 24 ml distilled water and 36 ml toluene was degassed and recharged with nitrogen. Then $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol) was added in the mixture as catalyst, and the mixture was degassed and recharged with nitrogen again. After stirred and refluxed at 90 °C for 48 h under nitrogen atmosphere, the mixture was extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was then purified by silica gel chromatography by the mixture of CH_2Cl_2 /petroleum ether as an eluent and pure dry white product is obtained (2.05g, yield: 80%). 1H NMR (500 MHz, $DMSO-d_6$, 25 °C, TMS): δ = 8.39 – 8.28 (m, 3H), 8.26 – 8.16 (m, 3H), 8.14 – 8.06 (m, 2H), 8.01 (d, J = 7.9 Hz, 1H), 7.67 – 7.53 (m, 6H), 7.46 – 7.37 (m, 5H), 7.37 – 7.26 (m, 7H), 7.25 – 7.18 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ = 146.712 (C), 141.096 (C), 138.524 (C), 137.260 (C), 137.072 (C), 134.523 (C), 131.492 (C), 131.219 (CH), 130.987 (C), 130.710 (C), 130.450 (CH), 129.534 (C), 129.250 (CH), 128.846 (CH), 128.599 (CH), 128.472 (CH), 128.426 (CH), 128.255 (CH), 128.063 (CH), 127.590 (CH), 127.479 (CH), 127.426 (CH), 126.717 (CH), 126.069 (CH), 125.178 (CH), 125.997 (C), 124.912 (CH), 124.666 (CH). MALDI-TOF MS (mass m/z): 573.52 [M^+]. Anal. calcd (%) for $C_{37}H_{26}N_2$: C 89.86, H 5.26, N 4.87; found (%): C 89.90, H 5.41, N 4.76.

2-(3-bromophenyl)-1,4,5-triphenyl-1H-imidazole (PIM-m-Br).

A mixture of benzil (1.68 g, 8.0 mmol), 3-bromo-benzaldehyde (0.93 ml, 8.0 mmol), aniline (2.91 ml, 32.0 mmol), ammonium acetate (3.08 g, 40.0 mmol) and acetic acid (30 mL) was refluxed under nitrogen at 120 °C oil bath for 2 h. After the mixture was cooled down and filtered, the solid product was washed with a 50 mL acetic acid/water mixture (1:1) and 50 mL water, dissolved in CH_2Cl_2 and dried with anhydrous sodium sulfate. It was then purified by silica gel chromatography using the mixture of CH_2Cl_2 /petroleum ether as an eluent and pure dry white product is obtained (3.59 g, yield: 80%). 1H NMR (500 MHz, $DMSO-d_6$, 25 °C, TMS): δ = 7.57 (t, J = 1.9 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.41 – 7.35 (m, 3H), 7.32 (dt, J = 6.3, 4.0,

1.9 Hz, 6H), 7.29 – 7.22 (m, 5H), 7.22 – 7.17 (m, 1H). MALDI-TOF MS (mass m/z): 450.06 (M^+).

1,4,5-triphenyl-2-(3-(pyren-1-yl)phenyl)-1H-imidazole (PIM-m-PY)

A mixture of PIM-m-Br (1.58 g, 3.5 mmol), 1-pyrenylboronic acid (0.98 g, 4.0 mmol), K_2CO_3 (4.42 g, 32.0 mmol), 16 ml distilled water and 24 ml toluene was degassed and recharged with nitrogen. Then $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol) was added in the mixture as catalyst, and the mixture was degassed and recharged with nitrogen again. After stirred and refluxed at 90 °C for 48 h under nitrogen atmosphere, the mixture was extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was then purified by silica gel chromatography by the mixture of CH_2Cl_2 /petroleum ether as an eluent and pure dry white product is obtained (1.72 g, yield: 75%). 1H NMR (500 MHz, $DMSO-d_6$, 25 °C, TMS): δ = 8.39 – 8.28 (m, 3H), 8.26 – 8.16 (m, 3H), 8.14 – 8.06 (m, 2H), 8.01 (d, J = 7.9 Hz, 1H), 7.68 – 7.52 (m, 6H), 7.47 – 7.37 (m, 5H), 7.37 – 7.26 (m, 7H), 7.25 – 7.18 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ = 146.890 (C), 140.974 (C), 138.436 (C), 137.222 (C), 137.128 (C), 134.458 (C), 131.461 (C), 131.173 (CH), 131.111 (CH), 130.930 (C), 130.834 (C), 130.676 (CH), 130.619 (C), 129.259 (CH), 128.587 (CH), 128.397 (CH), 128.212 (CH), 128.054 (CH), 127.665 (CH), 127.595 (CH), 127.432 (CH), 126.672 (CH), 126.007 (CH), 125.117 (CH), 125.099 (CH), 124.850 (CH), 124.548 (CH). MALDI-TOF MS (mass m/z): 573.35 [M^+]. Anal. calcd (%) for $C_{37}H_{26}N_2$: C 89.86, H 5.26, N 4.87; found (%): C 89.93, H 5.41, N 4.82.

S II Measurements and characterizations

General information: ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer, using tetramethylsilane (TMS) as the internal standard. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFRTM plus instrument. The compounds were characterized by a Flash EA 1112, CHNS elemental analysis instrument.

Photophysical measurements: UV-vis spectra of solutions were recorded on a Shimadzu UV-3100 Spectrophotometer. Steady-state fluorescence spectra and fluorescence lifetimes were collected with FLS980 Spectrometer. Photoluminescence quantum efficiencies (PLQYs) were measured using an integrating sphere apparatus.

Solutions were placed in 1 cm path length quartz cells, and crystals were fixed on the quartz plate in terms of steady-state fluorescence spectra and fluorescence lifetimes.

The radiative decay rate (k_r) and nonradiative decay rate (k_{nr}) were estimated according to the following formulas.

$$k_r = \frac{\text{PLQY}}{\tau}, \quad k_{nr} = \frac{1}{\tau} - k_r$$

Single crystal X-ray diffraction data: Crystal-G of IM-PY was obtained by slow evaporation of the mixture of tetrahydrofuran (THF) and methanol. Crystal-B of IM-PY was obtained in the mixture of dichloromethane (DCM) and methanol or in the mixture of DCM and hexane. Single crystal of PIM-m-PY was obtained by slow evaporation of the mixture of THF and methanol. Single crystal of PIM-p-PY was obtained by slow evaporation of the mixture of DCM and methanol. All single crystals were prepared at room temperature. The diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-K α and control Software using the RAPID AUTO at 293 (± 2) °C. The crystal structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS programs. All the figures of crystal structures were presented using Mercury

1.4.1 Software. All angles and distances in crystal structures were measured using Mercury 1.4.1 Software.

Theoretical calculation: All the density functional theory (DFT) calculations were carried out using Gaussian 09 (version D.01) package on a PowerLeader cluster.^[1] Theoretical calculations of frontier molecular orbital were calculated using DFT. The optimization of excited-state geometries was carried out using time-dependent DFT (TD-DFT) at the level of M06-2X/6-31 G (d, p). Natural transition orbitals (NTOs) were performed using TD-DFT at the level of M06-2X/6-31 G (d, p).

Electrostatic potential was calculated using Gaussian 09 (version D.01) package. Multiwfn software was used to calculate the intermolecular interaction.^[2]

SIII Figures and tables

Table S1. Crystallographic data of IM-PY, PIM-p-PY and PIM-m-PY.

	IM-PY		PIM-p-PY	PIM-m-PY
	Crystal-B	Crystal-G		
crystal color	colorless	yellow	colorless	colorless
empirical formula	C ₃₈ H ₂₆ Cl ₂ N ₂	C ₃₇ H ₂₄ N ₂	C ₄₃ H ₂₈ N ₂	C ₄₃ H ₂₈ N ₂
formula weight	581.51	496.58	572.67	572.67
<i>T</i> [K]	293(2)	293(2)	293(2)	293(2)
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	P -1	P 2 ₁ /c	P 2 ₁ /c	P 2 ₁ /n
<i>a</i> [Å]	10.2848(10)	14.7742(5)	16.209(2)	9.8428(4)
<i>b</i> [Å]	12.5366(11)	10.2059(4)	10.2021(13)	13.3440(5)
<i>c</i> [Å]	12.8773(12)	17.1834(6)	19.056(2)	23.3920(9)
α [°]	73.277(3)	90.00	90.00	90.00
β [°]	72.333(4)	95.511(2)	102.800(4)	95.265(2)
γ [°]	73.811(4)	90.00	90.00	90.00
<i>V</i> [Å ³]	1481.4(2)	2579.01(16)	3073.0(7)	3059.4(2)
<i>Z</i>	2	2	4	4
F(000)	604	1040	1200	1200
density [g/cm ³]	1.304	1.279	1.238	1.243
μ [mm ⁻¹]	0.250	0.572	0.072	0.072
reflections collected	4181	25539	78849	52854
unique reflections	4181	3560	7607	7575
<i>R</i> (int)	0.0452	0.0975	0.0513	0.0583
GOF	1.027	1.217	1.046	0.997
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0741	0.0717	0.0504	0.0500
ωR_2 [<i>I</i> > 2σ(<i>I</i>)]	0.1532	0.1487	0.1200	0.1188
<i>R</i> ₁ (all data)	0.1083	0.0924	0.0900	0.1086
ωR_2 (all data)	0.1680	0.1558	0.1536	0.1592
CCDC number	2006359	2006358	2006360	2006357

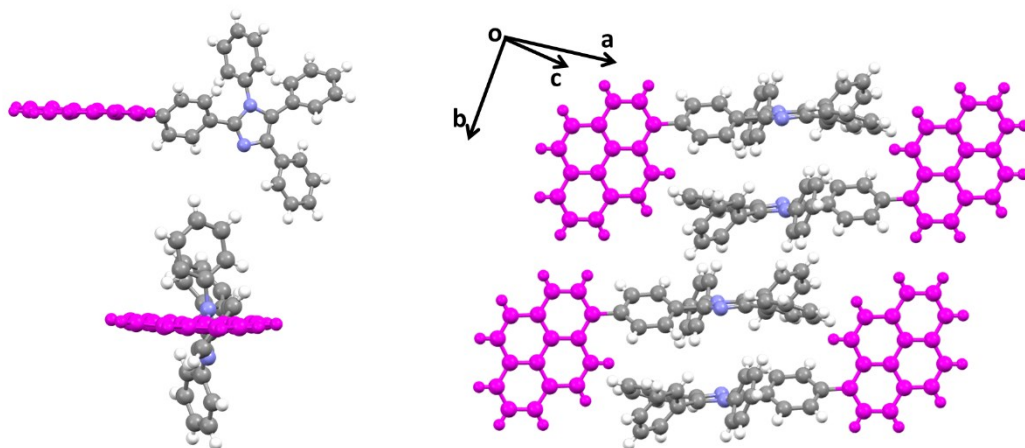


Figure S1. Crystal structure and molecular stacking in crystal of PIM-p-PY.

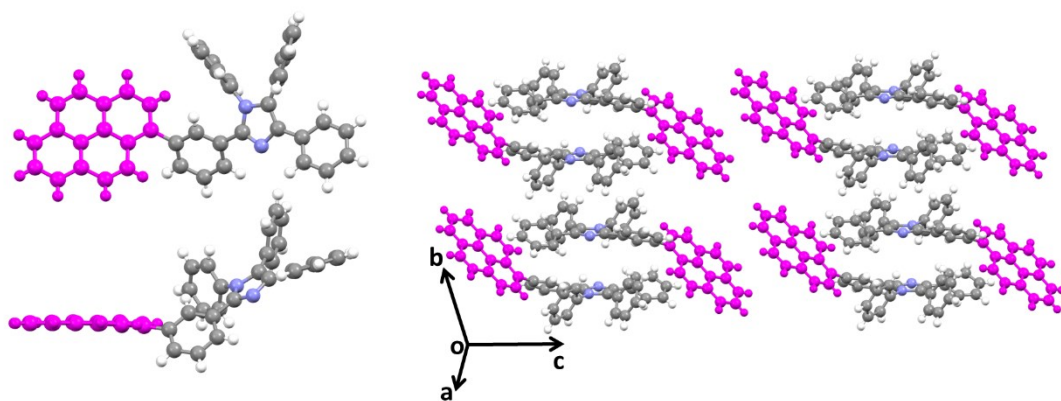


Figure S2. Crystal structure and molecular stacking in crystal of PIM-m-PY.

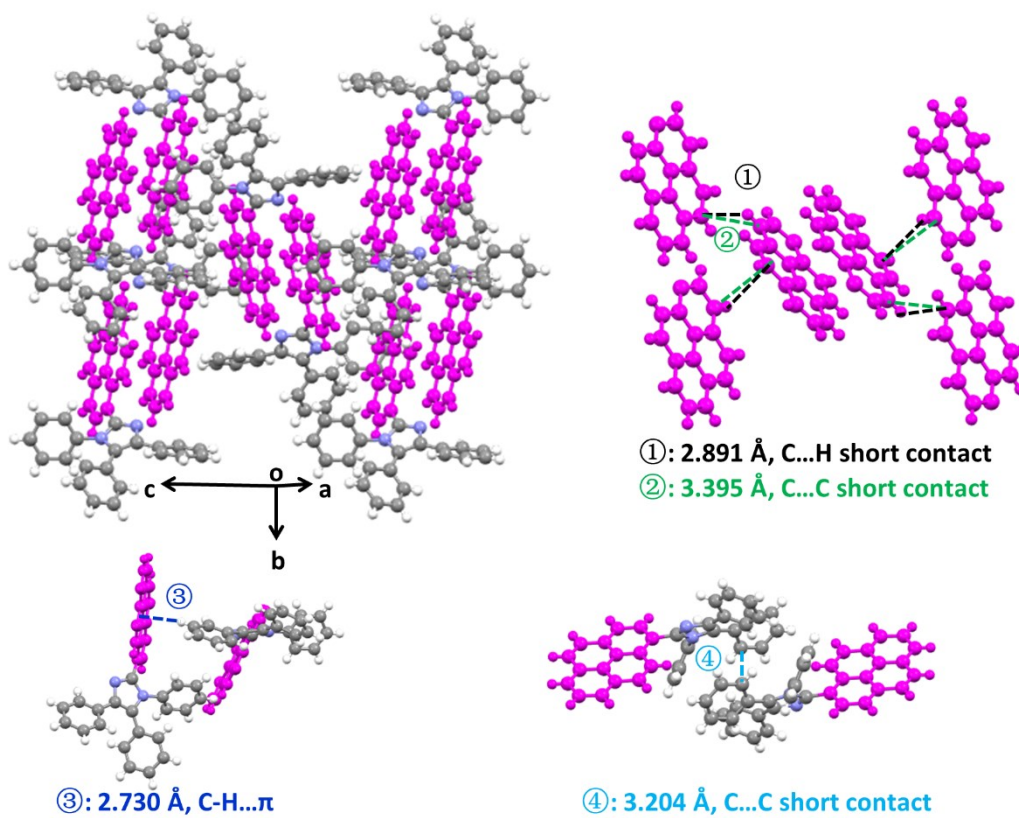


Figure S3. Crystal structure and intermolecular interaction in crystal-G of IM-PY.

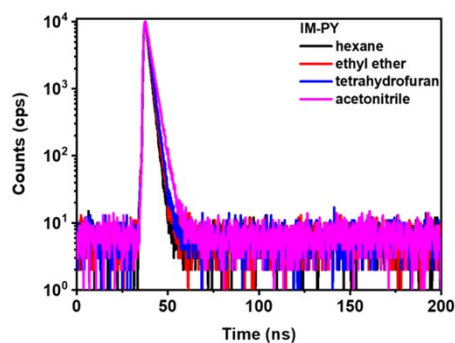


Figure S4. Time-resolved spectra of IM-PY in different solvents.

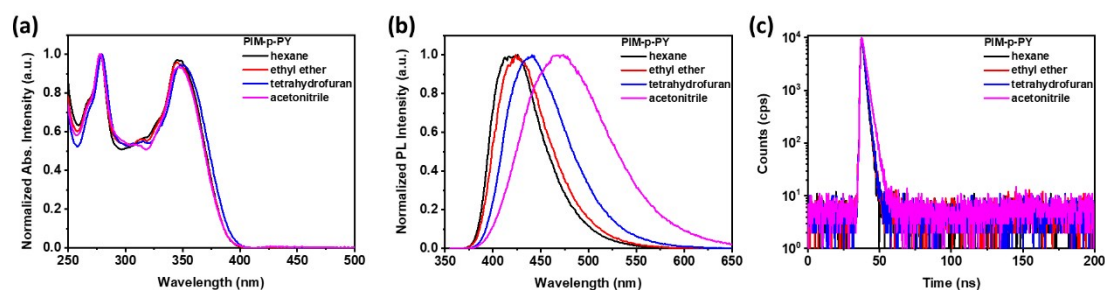


Figure S5. (a) Absorption spectra, (b) emission spectra and (c) time-resolved spectra of PIM-p-PY in different solvents.

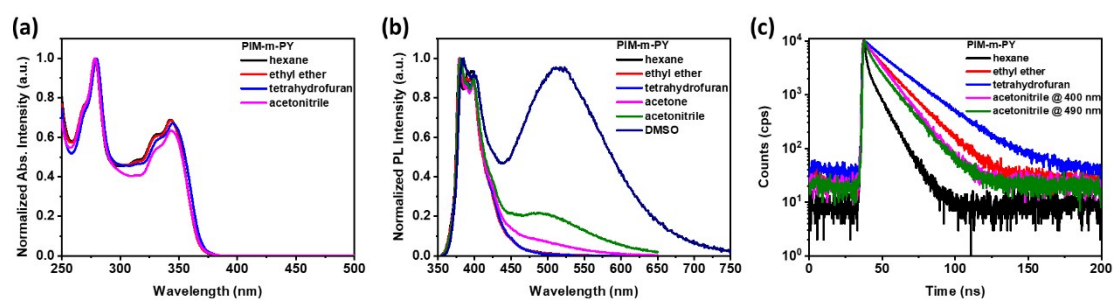


Figure S6. (a) Absorption spectra, (b) emission spectra and (c) time-resolved spectra of PIM-m-PY in different solvents.

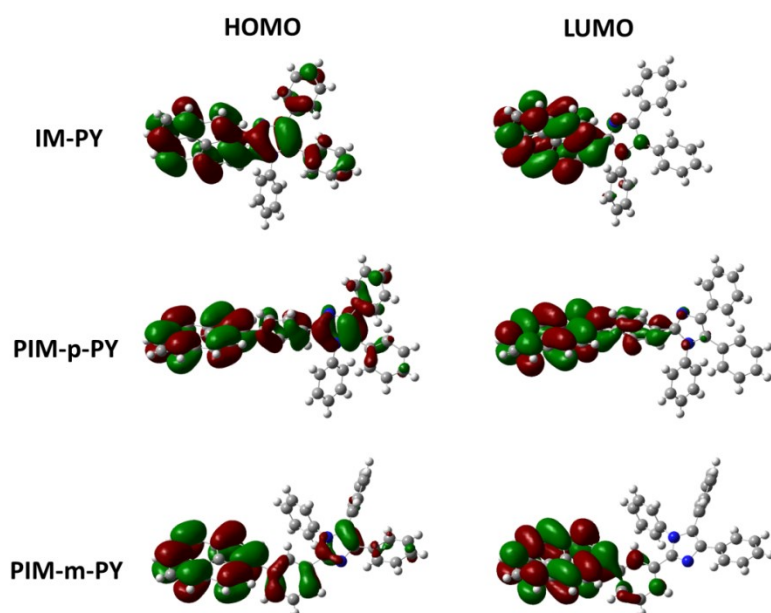


Figure S7. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of IM-PY, PIM-p-PY and PIM-m-PY, on basis of molecular conformation in crystal.

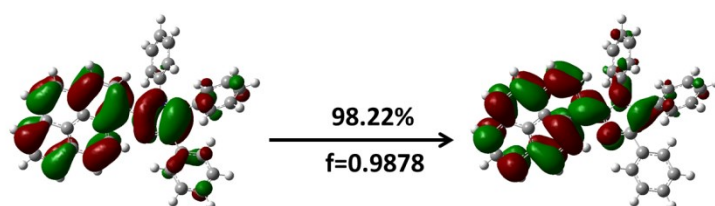


Figure S8. Emission NTO of IM-PY based on optimized excited-state geometry.

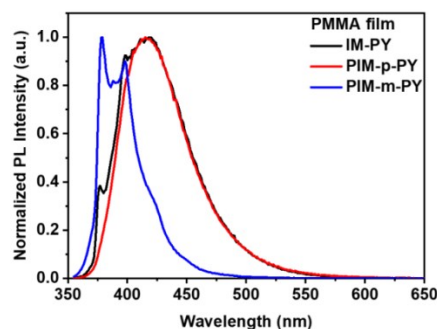


Figure S9. Emission spectra of 1% weight of IM-PY, PIM-p-PY and PIM-m-PY doped in polymethyl methacrylate (PMMA) film.

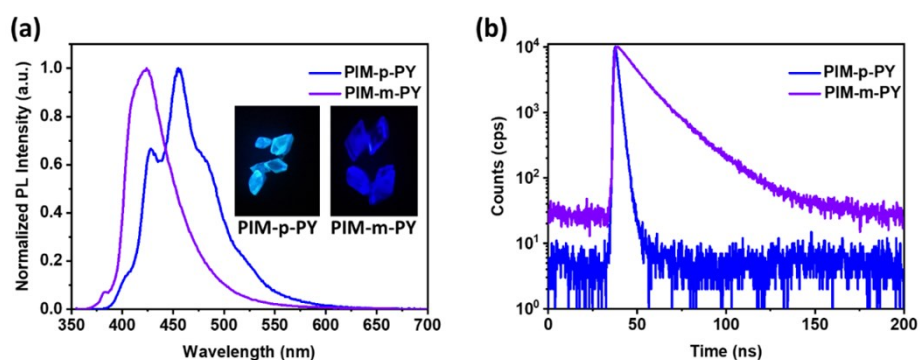


Figure S10. (a) Emission spectra and (b) time-resolved spectra of PIM-p-PY and PIM-m-PY crystals. PLQYs of PIM-p-PY and PIM-m-PY crystals are 30% and 26%, respectively. Lifetime of PIM-p-PY crystal is 1.78 ns, and lifetime of PIM-m-PY crystal is 9.95 ns (49.34%) and 20.95 ns (50.66%).

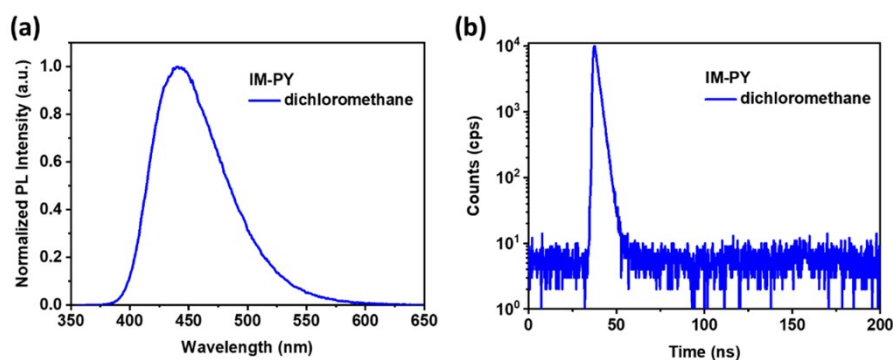


Figure S11. (a) Emission spectra and (b) time-resolved spectra of IM-PY in DCM solvent. Lifetime of IM-PY in DCM solvent is 2.08 ns.

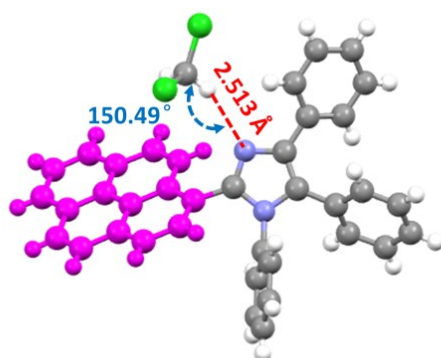


Figure S12. Hydrogen bond between DCM and IM-PY.

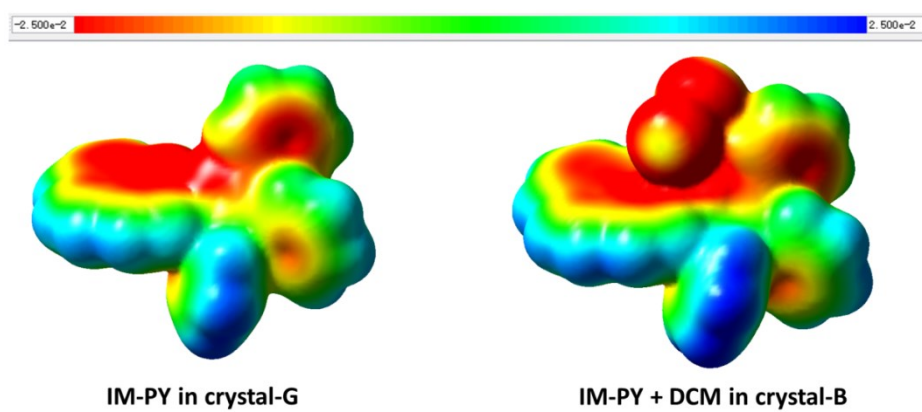


Figure S13. Electrostatic potential of IM-PY in crystal-G and IM-PY+DCM in crystal-B.

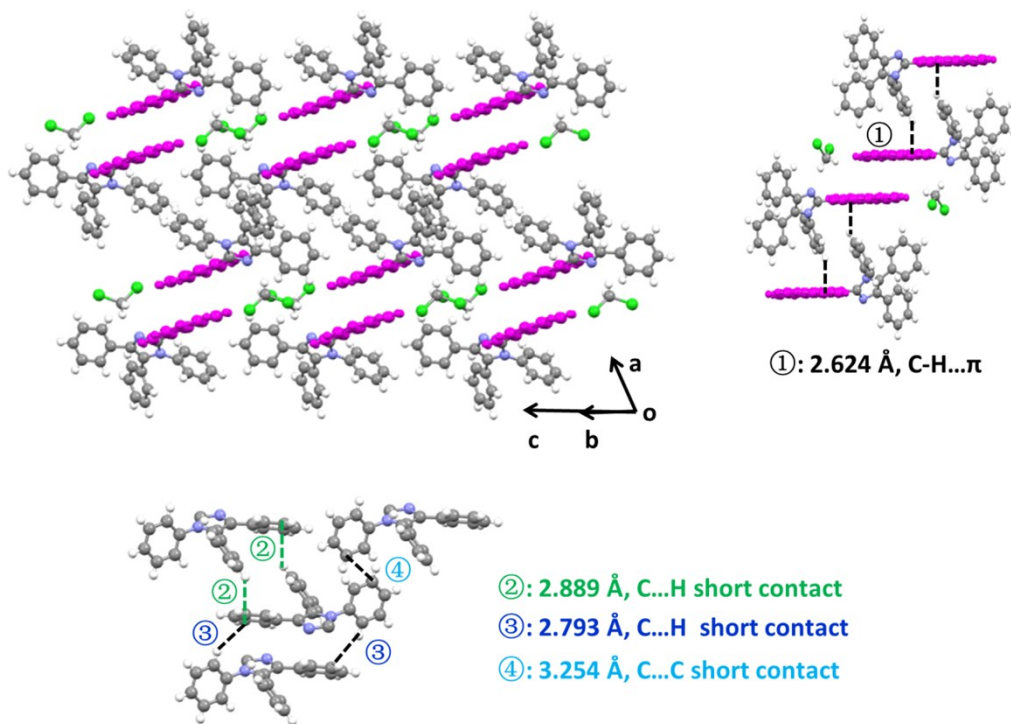


Figure S14. Crystal structure and intermolecular interaction in crystal-B of IM-PY.

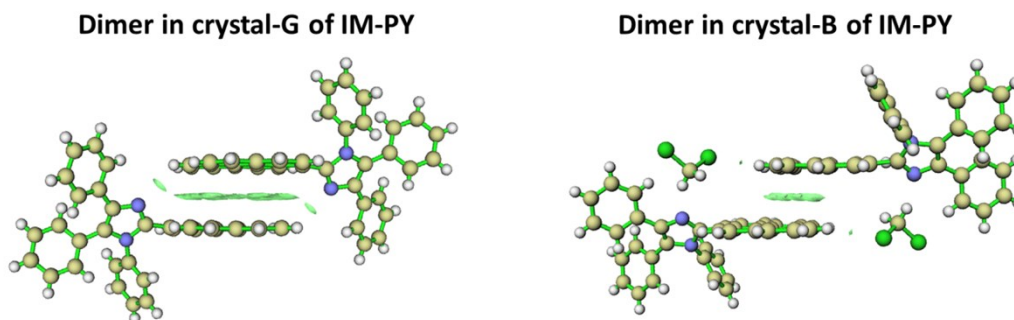


Figure S15. Calculation of intermolecular interaction using Multiwfn software.

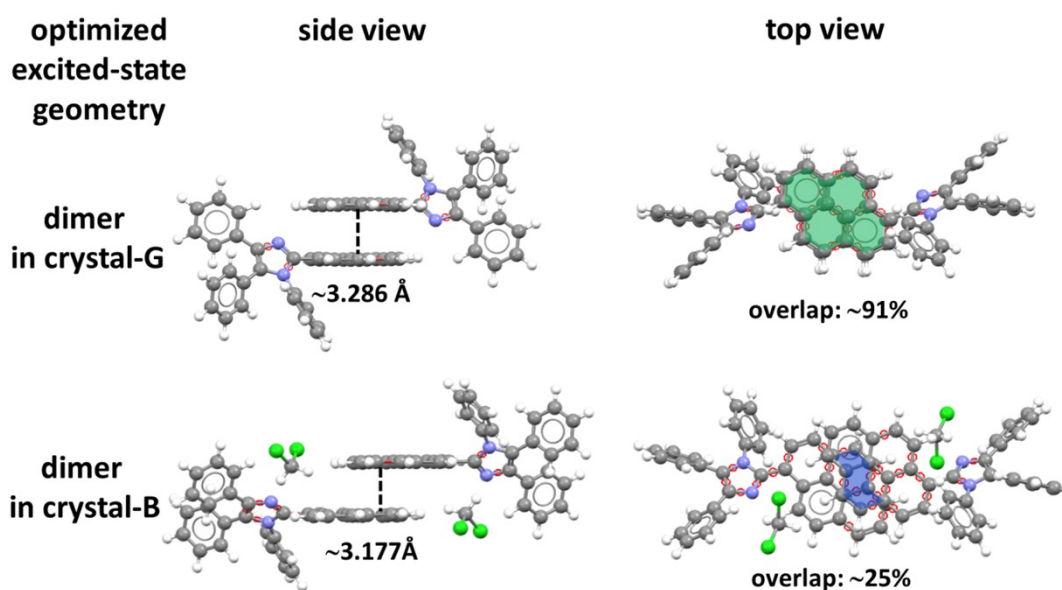


Figure S16. Optimized excited-state geometries of dimers in crystal-B and crystal-G using Gaussian 09 (version D.01) package.

Table S2. Comparison between calculated emission wavelength of pyrene dimer and experimental result.

Sample	Emission wavelength (nm)	
	Theoretical calculation	Experimental measurement
Dimer in crystal-B	406	418 , 443 , 475
Dimer in crystal-G	497	494

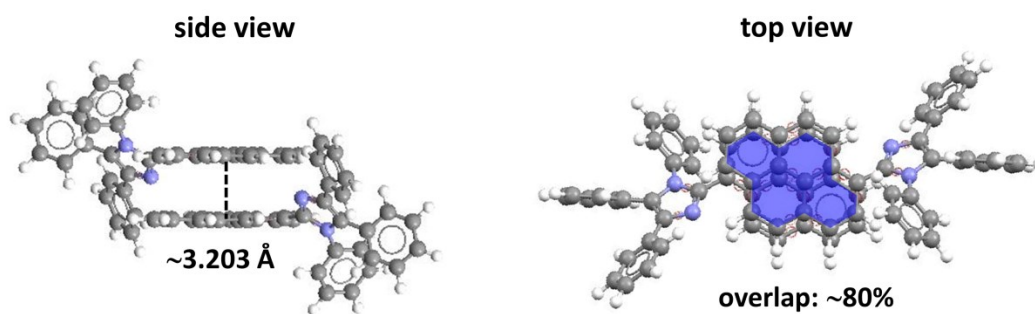


Figure S17. Optimized excited-state geometry of dimer in crystal-B. DCM molecules were removed from crystal-B to further optimize the excited-state geometry. In this case, the calculated emission wavelength is 495 nm and $f=0.0000$, indicating the excimer properties. The result demonstrates that DCM molecules increase the steric hindrance of substituents to prevent two pyrene units from sliding along pyrene plane.

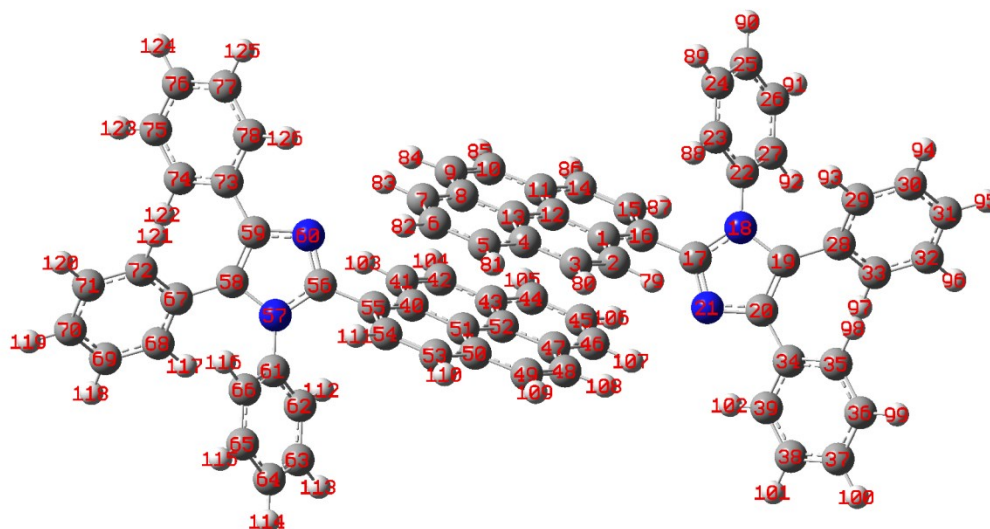


Figure S18. Labeled atoms for the calculation of transition density matrix (TDM) map of dimer in crystal-G. We ordered the atoms by labeling the main backbone (pyrene moiety) first and then the substituent (imidazole moiety) from one IM-PY molecule to the other IM-PY molecule. Since hydrogen atoms usually have little contribution to the transitions we are interested in, they are usually ignored by default.

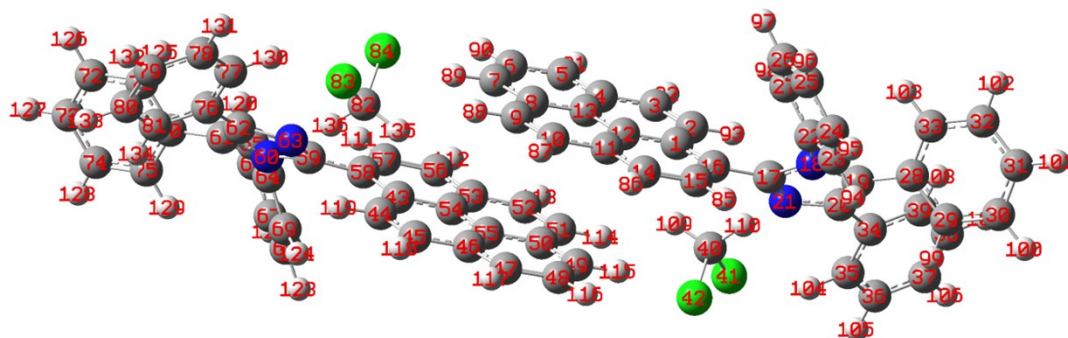


Figure S19. Labeled atoms for the calculation of TDM map of dimer in crystal-B.

SIV Reference

- [1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, **2013**.
- [2] T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.