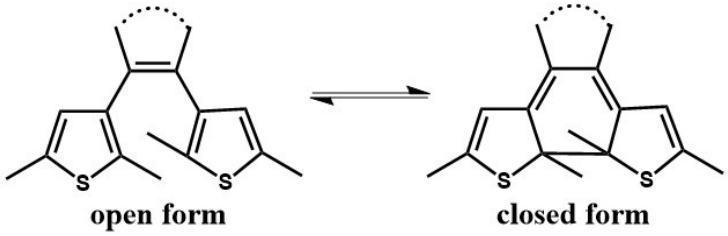
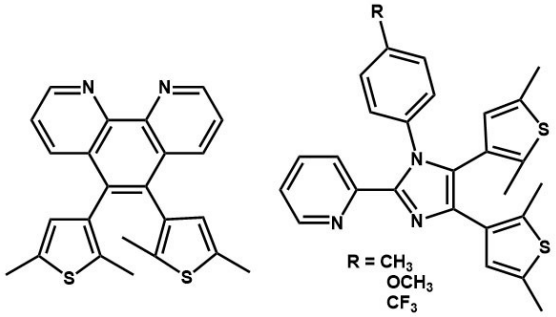
Electronic Supporting Information



Scheme S1 Structural transition between open form and closed form for dithienylethene (DTE).



Scheme S2 The molecular structures of the reported DTE-based N^N ancillary ligands in references 23 and 25 in the main text.

Table S1 Crystallographic data and refinement for **1** and **2**·C_7H_8

	1	**2**·C_7H_8
Formula	$C_{32}H_{27}N_4F_8PS_2Pt$	$C_{39}H_{37}N_4F_6PS_2Pt$
M	909.75	965.90
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
T /K	296(2)	193(2)
a /Å	9.0408(5)	7.2607(3)
b /Å	17.9156(8)	27.1529(10)
c /Å	19.9292(9)	18.6030(8)
β /°	96.929(2)	99.488(2)
V/Å^3	3204.4(3)	3617.4(3)
Z	4	4
D_c /g cm^{-3}	1.886	1.774
F(000)	1776	1912
GooF on F^2	1.036	1.047
R_1, wR_2 [$I>2\sigma(I)$][a]	0.0378, 0.0758	0.0390, 0.0856
R_1, wR_2 (all data)[a]	0.0601, 0.0823	0.0531, 0.0914
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	1.011, -1.266	1.029, -1.052

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond lengths (Å) and bond angles (°) for **1**

Pt1-C1	2.002(5)	Pt1-N3	2.111(4)
Pt1-N1	2.010(4)	N3-C17	1.346(6)
Pt1-N2	2.040(4)	N4-C17	1.358(6)
C1-Pt1-N1	79.75(19)	C7-N1-Pt1	117.1(3)
C1-Pt1-N2	101.30(18)	C12-N2-Pt1	127.2(4)
N1-Pt1-N2	178.32(18)	C16-N2-Pt1	115.0(3)
C1-Pt1-N3	176.99(17)	C18-N3-Pt1	142.6(3)
N1-Pt1-N3	101.14(16)	C17-N3-Pt1	109.9(3)
N2-Pt1-N3	77.88(15)	C2-C1-Pt1	130.5(4)
C11-N1-Pt1	124.1(3)	C6-C1-Pt1	112.2(4)

Table S3 Selected bond lengths (Å) and bond angles (°) for **2**·C_7H_8

Pt1-C1	2.008(5)	Pt1-N3	2.124(4)
Pt1-N1	2.011(5)	N3-C17	1.345(7)
Pt1-N2	2.050(4)	N4-C17	1.361(7)
C1-Pt1-N1	79.8(2)	C7-N1-Pt1	115.8(4)
C1-Pt1-N2	101.0(2)	C12-N2-Pt1	126.3(4)
N1-Pt1-N2	178.73(18)	C16-N2-Pt1	115.4(3)
C1-Pt1-N3	177.02(19)	C17-N3-Pt1	111.0(4)
N1-Pt1-N3	101.76(18)	C18-N3-Pt1	142.0(4)
N2-Pt1-N3	77.39(17)	C6-C1-Pt1	112.5(4)
C11-N1-Pt1	125.5(4)	C2-C1-Pt1	131.6(4)

Table S4 Photophysical properties of **1**, **2** and pbdtmi in CH_2Cl_2 at room temperature.

Compound	Medium	λ_{abs} (nm)	λ_{em} (nm)	Lifetime (ns)	quantum yield
1	CH_2Cl_2 (298 K)	306, 359 and a tail to 448	-	-	-
2	CH_2Cl_2 (298 K)	310, 363 and a tail to 456	-	-	-
pbdtmi	CH_2Cl_2 (298 K)	320	409	1.1 (85.5%), 3.4 (14.5%)	89.9%

Table S5 Luminescence data of **1**, **2** and pbdtmi in solid state at room temperature.

Compound	λ_{em} (nm)	Lifetime (ns)	quantum yield
1	579	7789 (62.9%), 3008 (35.5%), 333 (1.6%)	7.2%
2	551	4362 (86.9%), 845 (12.5%), 59 (0.6%)	6.8%
pbdtmi	393	5.2 (80.6%), 0.5 (19.4%)	1.0%

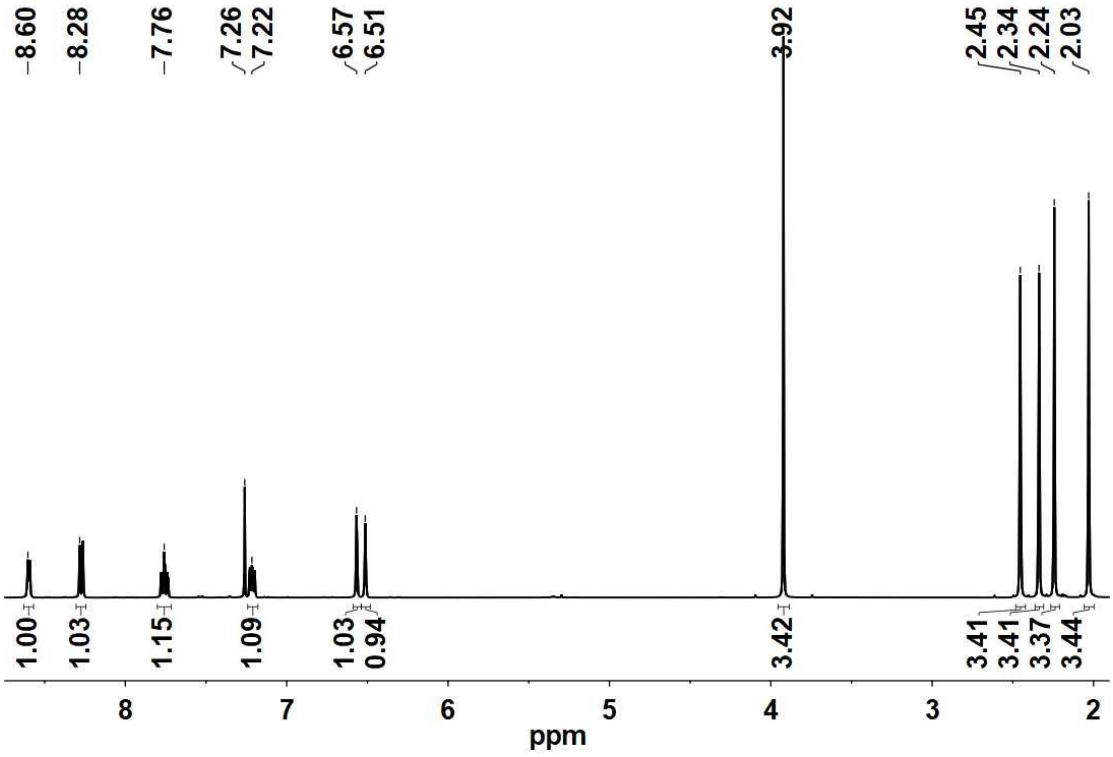


Fig. S1 The ^{1}H NMR of pbdtmi in $CDCl_3$.

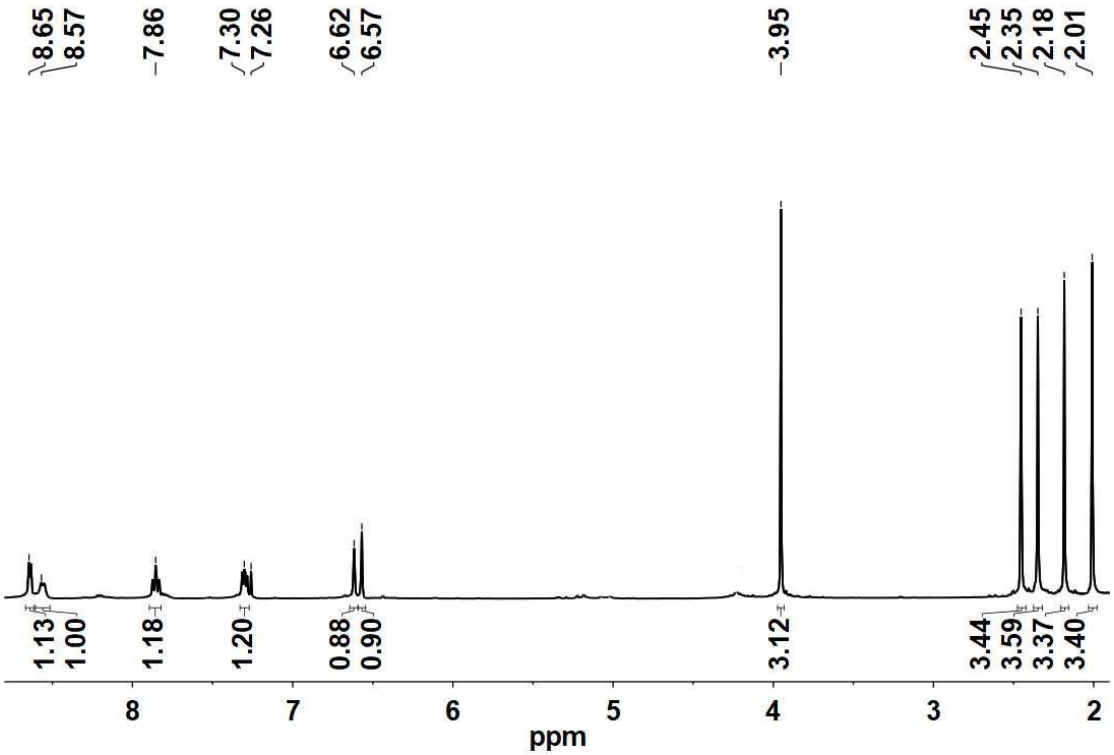


Fig. S2 The ^{1}H NMR of pbdtmi in $CDCl_3$ after irradiation for 30 min under 365 nm light [δ (ppm): 2.01-2.45 (4s, 12H from four -CH_3 groups attached to two thiophene rings), 3.95 (s, 3H from a -CH_3 group attached to the imidazole unit in pbdtmi), 6.57 and 6.62 (2s, 2H from two thiophene rings), 7.30 (t, J = 6.2, 1H), 7.86 (t, J = 7.8, 1H), 8.57 (d, J = 6.8, 1H) and 8.65 (d, J = 4.8, 1H) (7.30-8.65, total 4H from a pyridyl unit in pbdtmi).]

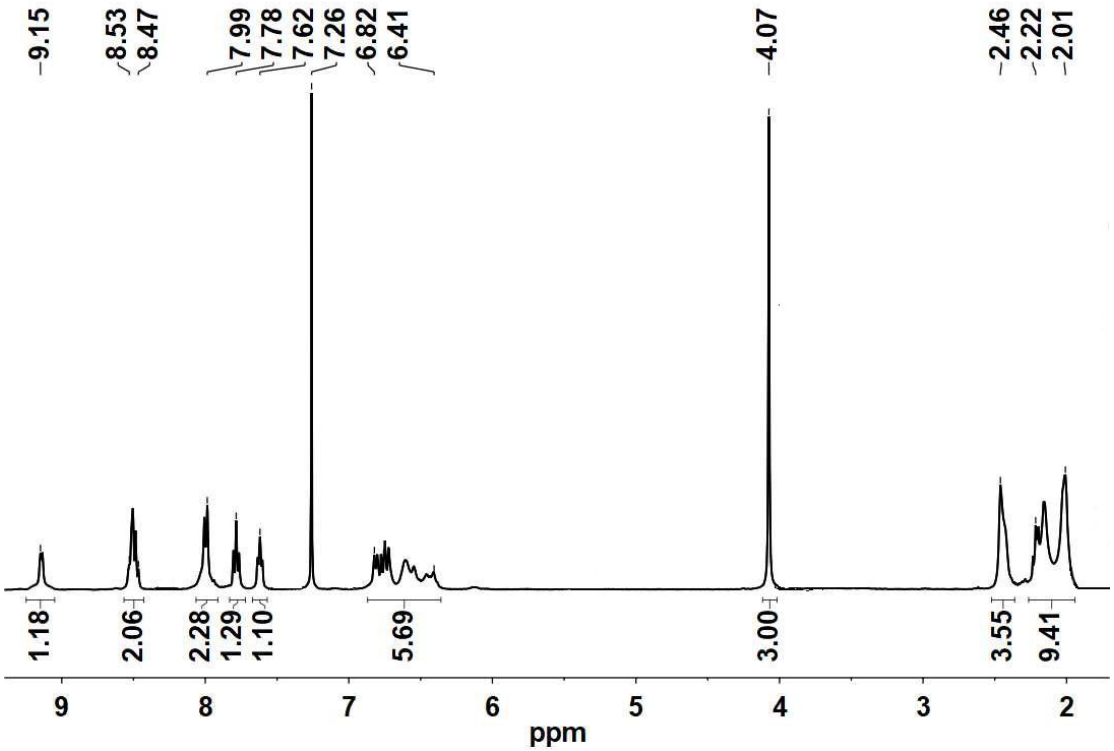


Fig. S3 ^{1}H NMR of **1** in $CDCl_3$

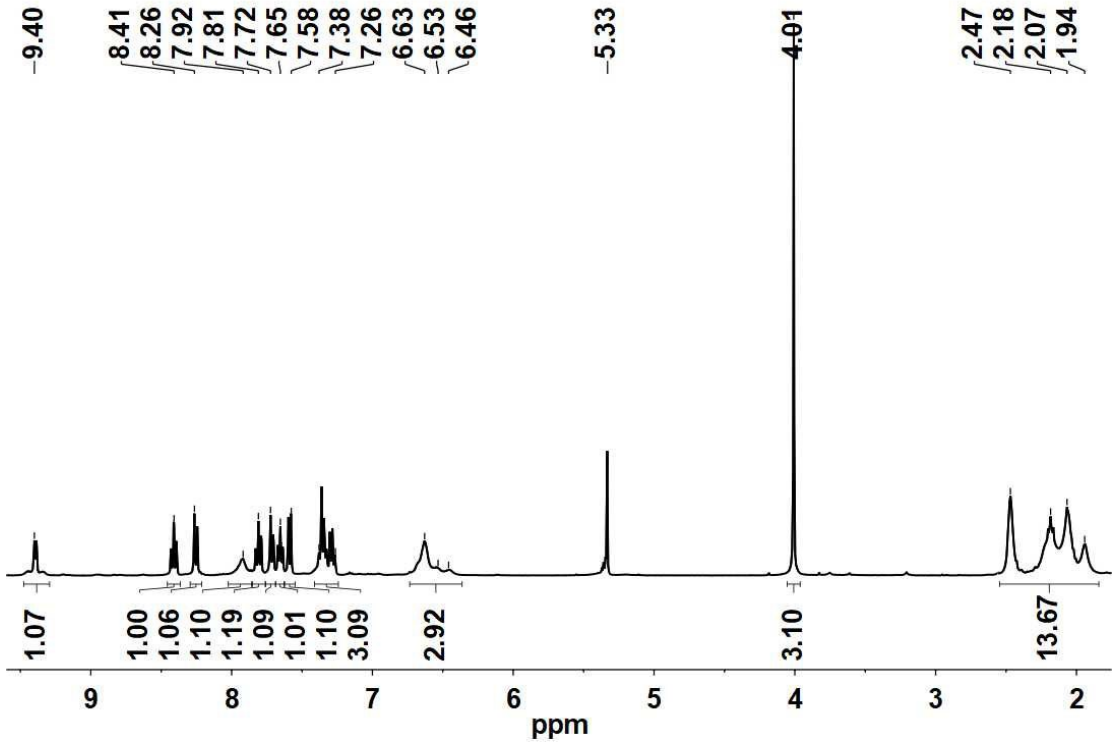


Fig. S4 ^{1}H NMR of **2** in CD_2Cl_2.

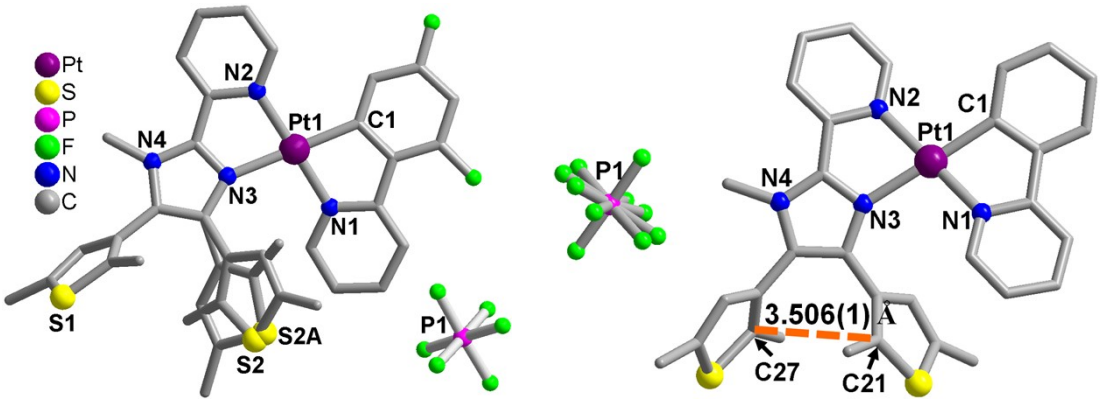


Fig. S5 Molecular structures of **1** (left) and **2** (right). All H atoms attached to carbon atoms are omitted for clarity. One of two thiophene groups in **1** and the PF_6^- ion in **2** are disordered.

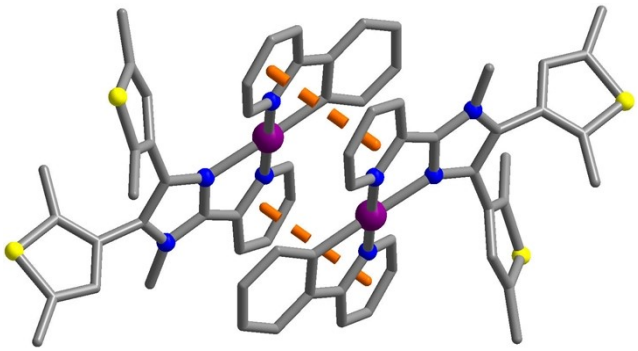


Fig. S6 Supramolecular dimer structure in complex **2**·C_7H_8.

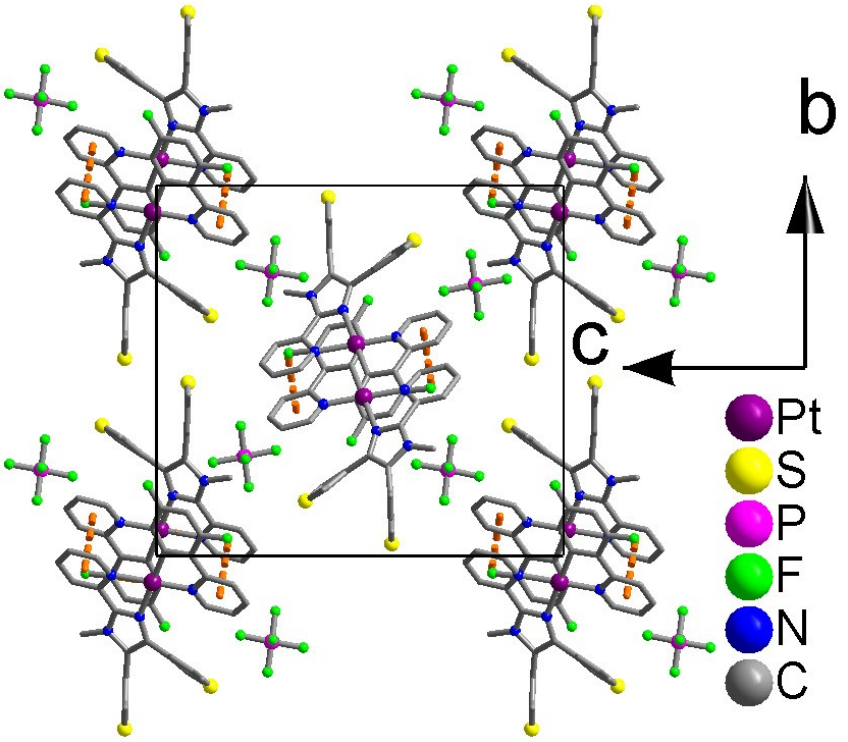


Fig. S7 Packing structure of **1**. The disordered states of thiophene groups in this Fig. have not been shown for clarity.

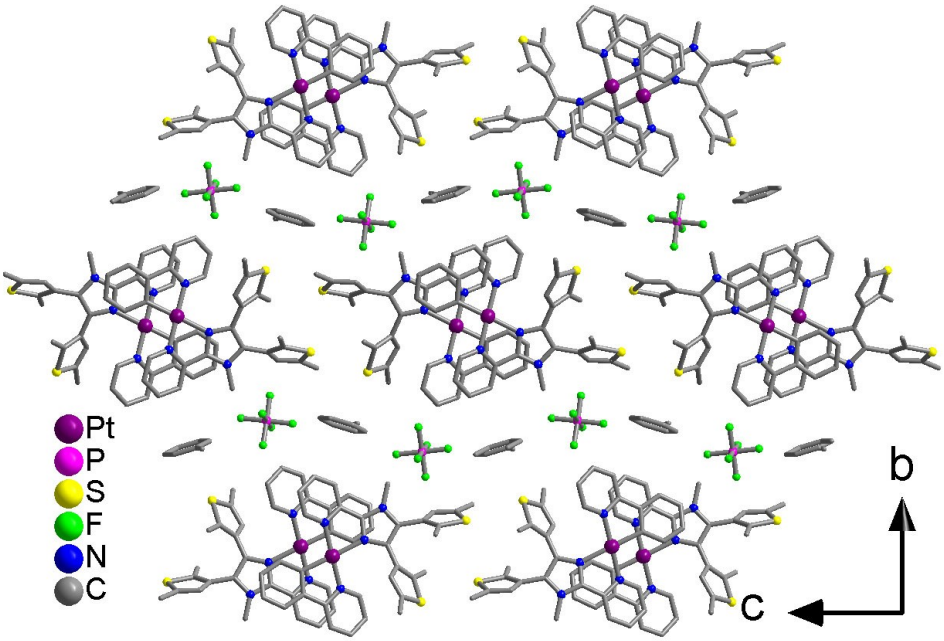


Fig. S8 Packing structure of **2**·C_7H_8. The toluene molecules and PF_6^- ions in this structure are disordered. However, their disordered states have not been shown in this figure for clarity.

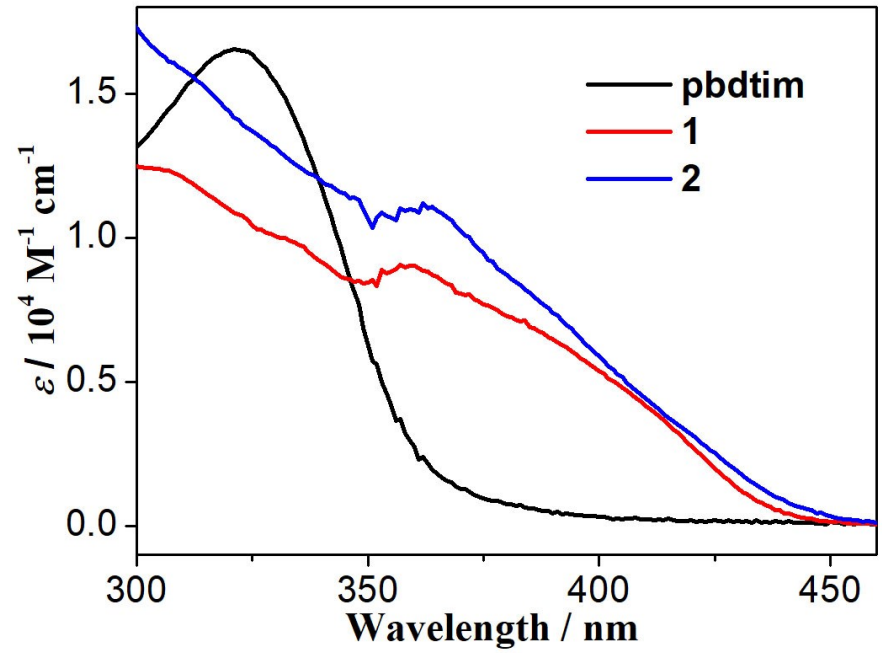


Fig. S9 UV-v is spectra of pbdtmi, **1** and **2** in CH_2Cl_2.

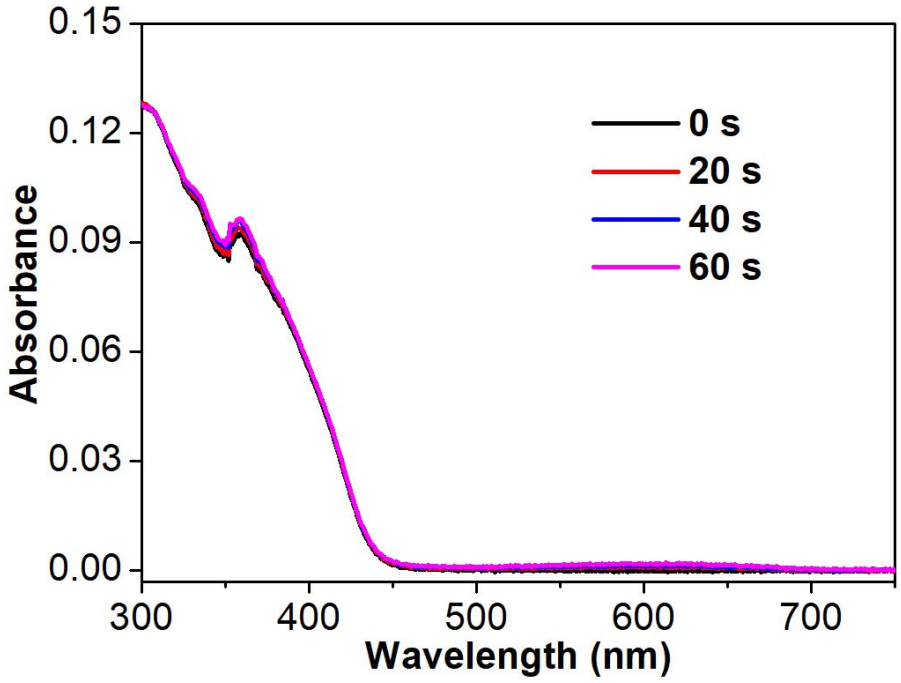


Fig. S10 Absorption spectra changes of **1** in CH_2Cl_2 solution ($c = 1.0 \times 10^{-5}$ M) upon UV irradiation ($\lambda = 365$ nm) for 0–60 seconds.

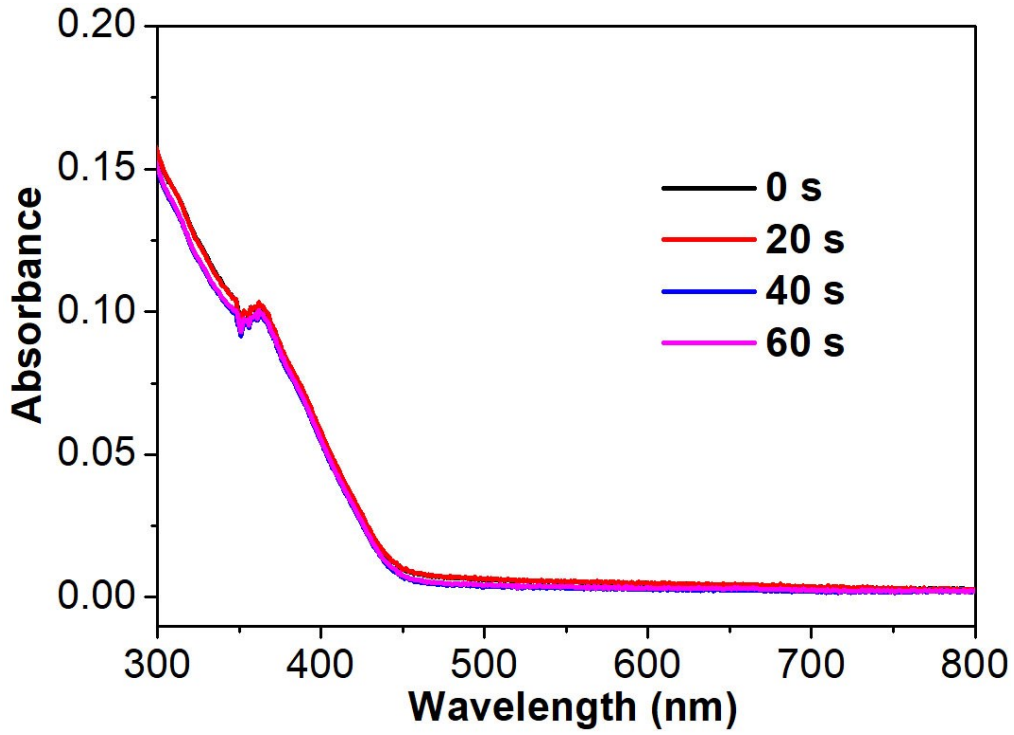


Fig. S11 Absorption spectra changes of **2** in CH_2Cl_2 solution (c = 1.0 × 10^{-5} M) upon UV irradiation (λ = 365 nm) for 0–60 seconds.

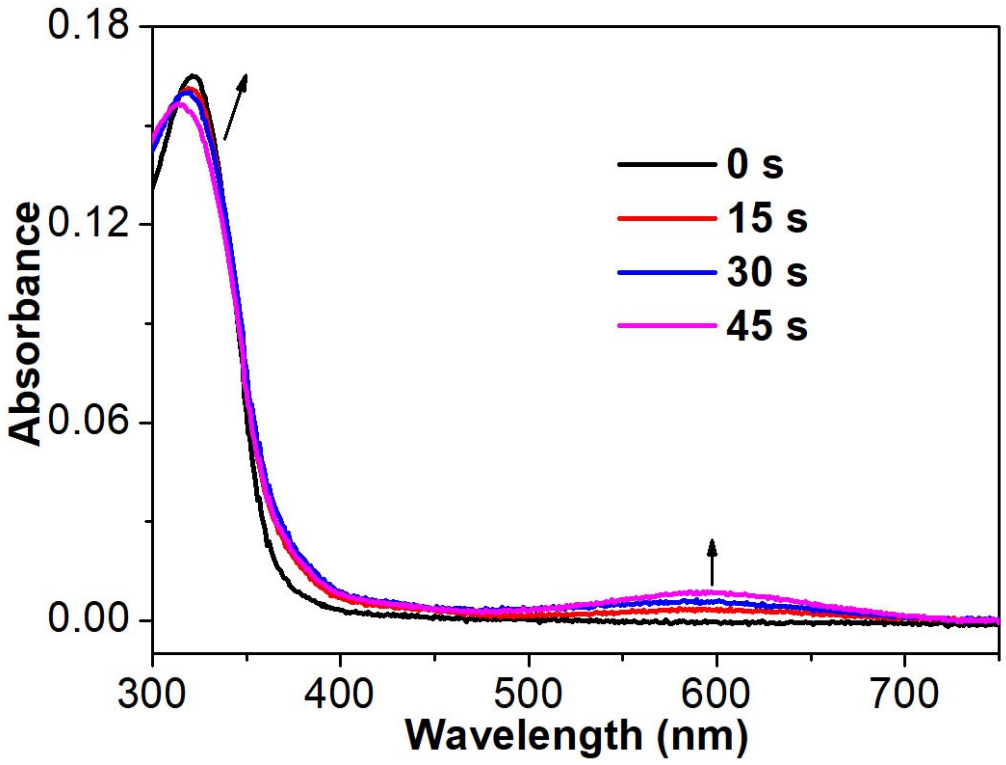


Fig. S12 Absorption spectra changes of pbdtmi in CH_2Cl_2 solution (c = 1.0 × 10^{-5} M) upon UV irradiation (λ = 325 nm) for 0–45 seconds.

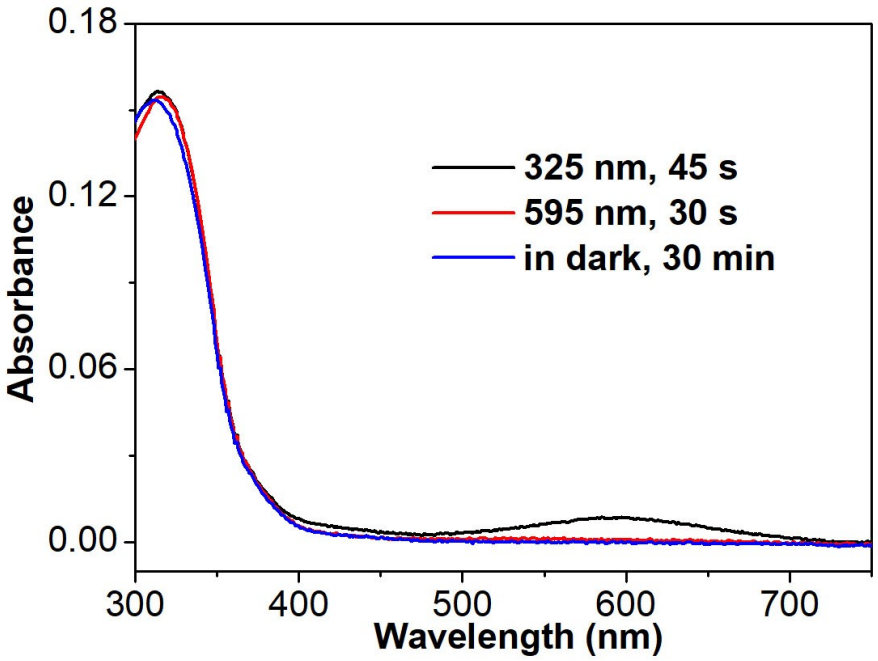


Fig. S13 Black line: irradiating (λ = 325 nm) the CH_2Cl_2 solution of pbdtmi in CH_2Cl_2 for 45 seconds; red line: irradiating (λ = 595 nm) the solution corresponding to black line for 30 seconds; blue line: placing the solution corresponding to black line in the dark for 30 minutes.

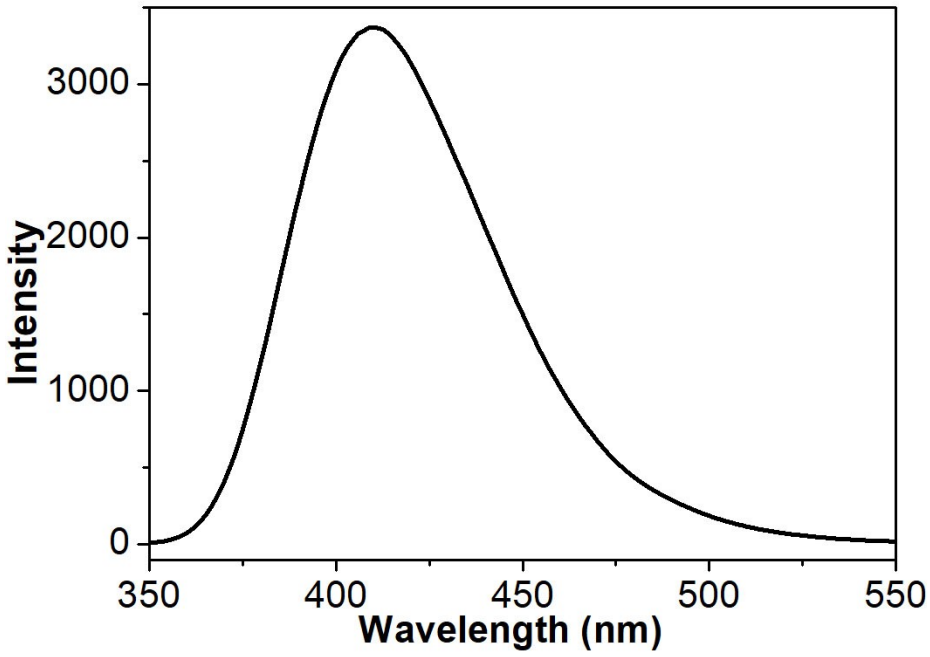


Fig. S14 Luminescence spectrum of pbdtmi in CH_2Cl_2 solution (c = 1.0×10^{-4} M, λ_{ex} = 336 nm).