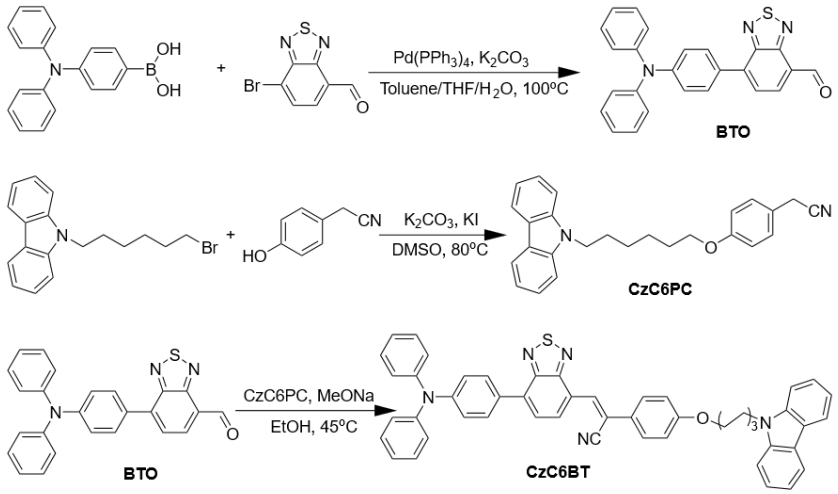
Synthesis



Scheme S1 The synthetic route of **BTO**, **CzC6PC** and **CzC6BT**.

7-(4-(diphenylamino)phenyl)benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (BTO)

The intermediate 7-(4-(diphenylamino)phenyl)benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde was synthesized by reference[1] to literature methods, (4-(diphenylamino)phenyl)boronic acid (1.74 g, 6 mmol), 7-bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde (1.22 g, 5 mmol), Tetrakis(triphenylphosphine)palladiu (0.06 g, 0.05 mmol) and K_2CO_3 (1.38 g, 10 mmol) were placed in a 250 mL round-bottom flask. The mixed solvent of toluene (25 mL), tetrahydrofuran (10 mL) and Water (2 mL) was added, and the mixture was vigorously stirred at 100 °C for 12 h under nitrogen. Water (30 mL) was added to quench the reaction, the mixture was then extracted with dichloromethane. The organic solution was extracted with dichloromethane (3 × 50 mL) followed by purification by column chromatography on silica gel with petroleum ether/dichloromethane (1: 1) as the eluent to offer a red powder. The desired compound was obtained in 83% yield (1.70 g). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.75 (s, 1H), 8.27 (d, *J* = 7.4 Hz, 1H), 7.93 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.83 (d, *J* = 7.4 Hz,

1H), 7.32 (t, *J* = 7.3 Hz, 4H), 7.24 – 7.16 (m, 6H), 7.11 (t, *J* = 7.3 Hz, 2H).

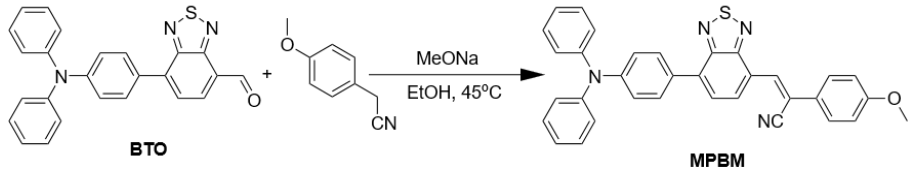
2-(4-((6-(9*H*-carbazol-9-yl)hexyl)oxy)phenyl)acetonitrile (CzC6PC)

The intermediate 2-(4-((6-(9*H*-carbazol-9-yl)hexyl)oxy)phenyl)acetonitrile was synthesized by reference[2] to literature methods, 9-(6-bromohexyl)-9*H*-carbazole (3.30 g, 10 mmol), K_2CO_3 (1.38 g, 10 mmol) and KI (0.02 g, 0.15 mmol) were added to a solution of 4-hydroxyphenylacetonitrile (1.46 g, 11 mmol) in dry DMSO (40 mL) at room temperature. This mixture was stirred at 80 °C for overnight. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. The organic solution was extracted with ethyl acetate (3 × 50 mL) followed by purification by column chromatography on silica gel with petroleum ether/dichloromethane (4: 1) as the eluent to offer a white powder. The desired compound was obtained in 79% yield (3.02 g). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.87 (dd, *J* = 8.4, 1.3 Hz, 2H), 4.35 (t, *J* = 7.1 Hz, 2H), 3.92 (td, *J* = 6.4, 1.1 Hz, 2H), 1.95 (p, *J* = 7.2 Hz, 2H), 1.77 (p, *J* = 6.6 Hz, 2H), 1.60 – 1.42 (m, 4H).

(*Z*)-2-(4-((6-(9*H*-carbazol-9-yl)hexyl)oxy)phenyl)-3-(7-(4-(diphenyl amino)phenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)acrylonitrile (CzC6BT)

A mixture of BTO (1.22 g, 3 mmol) and CzC6PC (1.34 g, 3.5 mmol) in ethanol (HPLC grade, 30 mL) was stirred at room temperature for 5 min. And then, $NaOCH_3$ (0.270 g, 5 mmol) was added and stirred for 30 min. Finally, the mixture was heated and stirred at 45 °C for 12 h. The resulting powder was filtered and repeatedly washed with EtOH (~50 mL) and followed by purification by column chromatography on silica gel with petroleum ether/dichloromethane (1: 1) as the eluent to offer a red powder (1.90 g, 82%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.68 (dd, *J* = 7.6, 0.8 Hz, 1H), 8.42 (s, 1H), 8.12 (d, *J* = 7.7 Hz, 2H), 7.92 (dt, *J* = 8.7, 2.6 Hz,

2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.73 (dt, *J* = 8.9, 3.3 Hz, 2H), 7.47 (td, *J* = 8.2, 0.9 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 8.4 Hz, 4H), 7.24 (dd, *J* = 7.7, 1.0 Hz, 2H), 7.22 – 7.19 (m, 6H), 7.09 (td, *J* = 7.3, 1.2 Hz, 2H), 6.94 (dt, *J* = 8.8, 3.3 Hz, 2H), 4.35 (t, *J* = 7.1 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 1.94 (p, *J* = 7.2 Hz, 2H), 1.78 (p, *J* = 6.5 Hz, 2H), 1.53 (p, *J* = 15.1, 7.5 Hz, 2H), 1.48 (p, *J* = 6.9, 6.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 159.23, 154.05, 146.24, 139.39, 132.10, 129.07, 128.41, 126.57, 125.96, 125.57, 124.59, 124.20, 124.14, 122.60, 121.81, 121.40, 119.36, 117.75, 114.00, 111.30, 107.59, 76.31, 75.99, 75.67, 66.94, 41.91, 27.99, 27.92, 26.04, 24.89. ESI-MS m/z: Found 772.3062 $[M]^+$; ion formula $C_{51}H_{42}N_5OS^+$ requires 772.3110 $[M]^+$; Elemental analysis given N: 8.99%; C: 79.34%; H: 5.39%; S: 4.41%; Molecular formula $C_{51}H_{41}N_5OS$ requires N: 9.07%; C: 79.35%; H: 5.35%; S: 4.15%.



Scheme S2 The synthetic route of **MPBM**.

(*Z*)-3-(7-(4-(diphenylamino)phenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)-2-(4-methoxyphenyl)acrylonitrile (MPBM)

A mixture of BTO (0.815 g, 2 mmol) and 2-(4-methoxyphenyl)acetonitrile (0.441 g, 3 mmol) in methanol (20 mL) was stirred at room temperature for 5 min. And then, $NaOCH_3$ (0.216 g, 4 mmol) was added and stirred for 30 min. Finally, the mixture was heated and stirred at 45 °C for 12 h. The resulting powder was filtered and repeatedly washed with EtOH (~50 mL) and followed by purification by column chromatography on silica gel with petroleum ether/dichloromethane (1: 1) as the eluent to offer a red powder (0.823 g, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (dd, *J* = 7.7, 0.9 Hz, 1H), 8.45 (s, 1H), 7.94 (dt, *J* = 8.8, 2.8 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.79

(dt, *J* = 8.9, 3.1 Hz, 2H), 7.33 (td, *J* = 8.2, 1.9 Hz, 5H), 7.26 – 7.19 (m, 6H), 7.11 (td, *J* = 7.4, 0.9 Hz, 2H), 7.03 (dt, *J* = 8.9, 1.9 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.16, 148.66, 147.28, 135.20, 133.25, 130.11, 129.98, 129.45, 127.73, 127.64, 126.97, 126.80, 125.19, 123.64, 122.42, 118.30, 114.58, 112.28, 55.51. ESI-MS m/z: Found 537.1734 $[M]^+$; ion formula $C_{34}H_{25}N_4OS^+$ requires 537.1749 $[M]^+$. Elemental analysis given N: 10.26%; C: 75.85%; H: 4.54%; S: 6.38%; Molecular formula $C_{34}H_{24}N_4OS$ requires N: 10.44%; C: 76.10%; H: 4.51%; S: 5.97%.

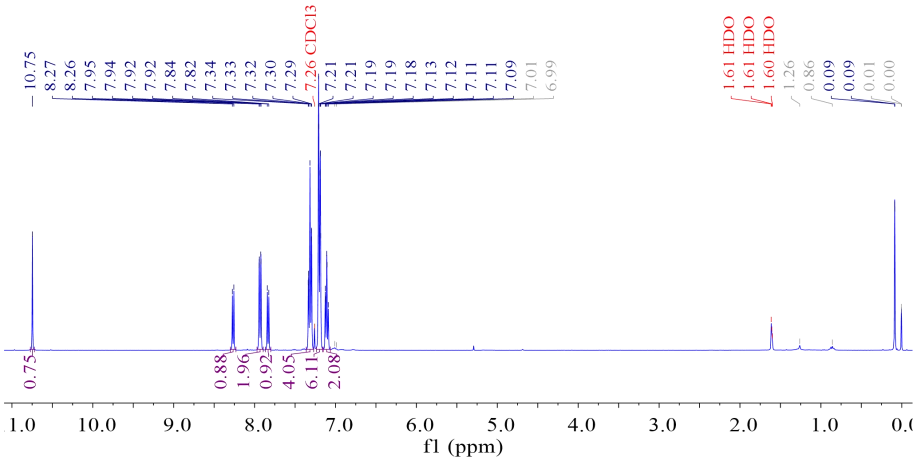


Fig. S1 ^{1}H-NMR spectra of **BTO**.

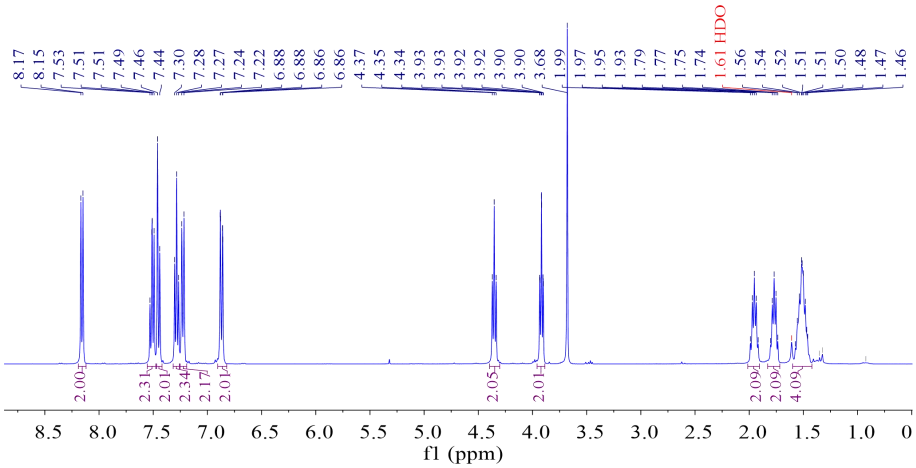


Fig. S2 ^{1}H-NMR spectra of **CzC6PC**.

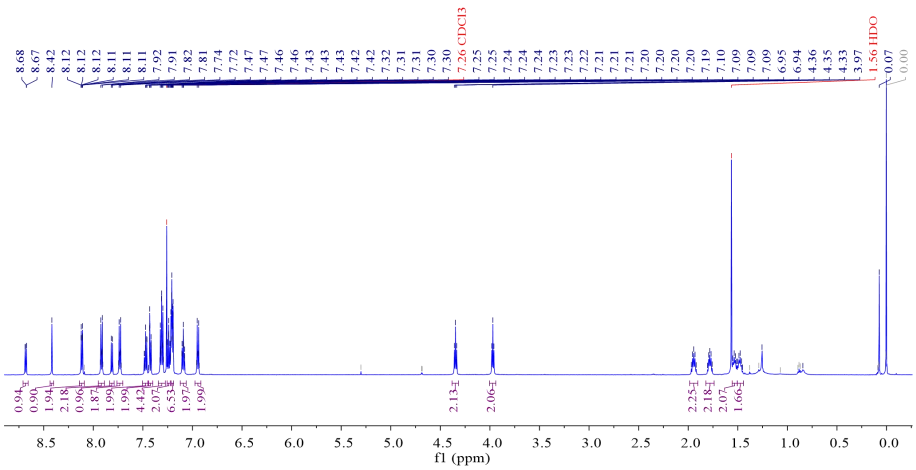


Fig. S3 ^{1}H-NMR spectra of **CzC6BT**.

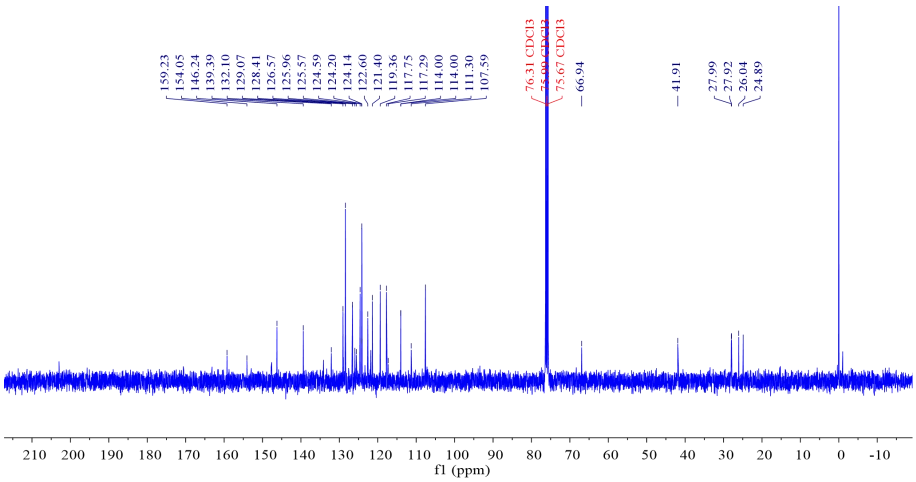


Fig. S4 ^{13}C-NMR spectra of **CzC6BT**.

Formula	Ion Formula	Calc. m/z	m/z	Diff(ppm)
$C_{51}H_{40}N_5OS$	$[M+H]^+$	772.3110	772.3062	6.2
$C_{51}H_{40}N_5OS$	$[M+Na]^+$	794.2930	794.2914	2.0

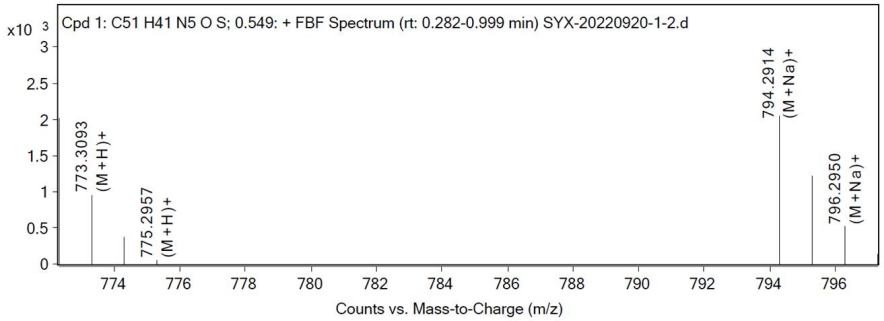


Fig. S5 ESI-MS spectrum of **CzC6BT**.

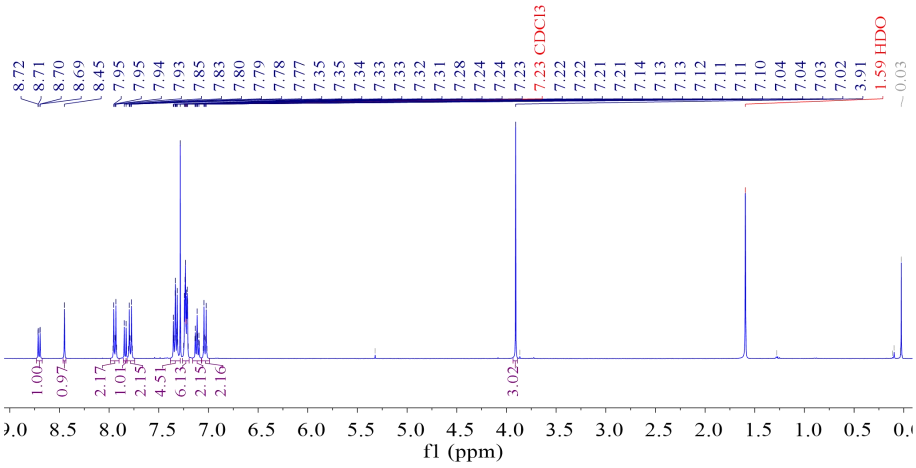


Fig. S6 ^{1}H-NMR spectra of **MPBM**.

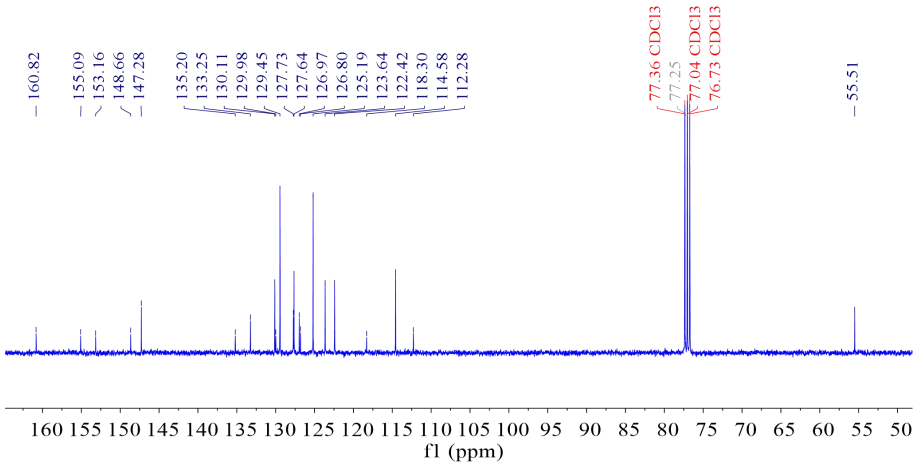


Fig. S7 ^{13}C-NMR spectra of **MPBM**.

Formula	Ion Formula	Calc. m/z	m/z	Diff(ppm)
$C_{34}H_{24}N_4OS$	$[M+H]^+$	537.1749	537.1734	2.8
$C_{34}H_{24}N_4OS$	$[M+Na]^+$	559.1568	559.1549	3.4

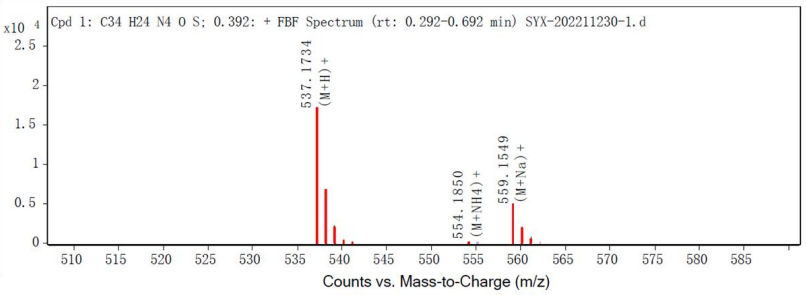


Fig. S8 ESI-MS spectrum of **MPBM**.

The change in magnitude of the dipole moment between the ground and excited states, that is, $\Delta\mu = |\mu_e - \mu_g|$ can be estimated using the Lippert–Mataga equation

$$hc(v_a - v_f) = hc(v_a^0 - v_f^0) + \frac{2(\mu_e - \mu_g)^2}{a_0^3} f(\varepsilon, n)$$

Where a_0 is the cavity radius in which the solute resides, estimated to be 7.21 Å. μ_g is the ground-state dipole moment, estimated to be 1.00 D (B3LYP at the basis set level of 6-31G(d, p)), μ_e is the excited state dipole moment. h and c are Planck's constant and the speed of light, respectively, and $f(\varepsilon, n)$ is the orientation polarizability, defined as

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

Where ε is the static dielectric constant and n is the optical refractivity index of the solvent. Through the analysis of the fitted line in solvents, its corresponding μ_e was calculated to be 21.1 D with the slope of 15032 according to Lippert-Mataga equation.

Table S1 Detailed photo-physical data of **CzC6BT** in the different solvents.

Solvents	f	λ_{abs} nm	λ_{flu} nm	ν_a cm^{-1}	ν_f cm^{-1}	ν_a-ν_f cm^{-1}	PLQY
Hexane (Hex)	0	485	567	20619	17637	2982	1
Butyl ether (NBE)	0.096	491	595	20367	16806	3559	0.973
Isopropyl ether (IPE)	0.145	488	607	20491	16474	4017	0.956
Ethyl ether (DEE)	0.167	482	624	20747	16026	4721	0.894
Ethyl acetate (EA)	0.200	477	654	20964	15291	5674	0.718
Tetrahydrofuran (THF)	0.210	482	662	20747	15106	5641	0.743
Dichloromethane (DCM)	0.218	483	670	20704	14925	5779	0.656
Acetone (CP)	0.284	475	695	21053	14388	6664	0.105
Acetonitrile (ACN)	0.305	467	722	21413	13850	7562	0.037

Table S2 Optical properties of **CzC6BT** in different states.

	Peak (nm)	φ_F (%)	τ[a] (ns)	k_f[b] (10^7 s^{-1})	k_{nf}[c] (10^7 s^{-1})
Crystal-a	680	40.1	4.38	9.16	13.68
Crystal-b	670	21.0	2.48	8.47	31.85
Molten	690	48.5	3.92	12.37	13.14
Spin-coated	640	20.0	2.36	8.47	33.90

[a] τ = the mean lifetime;
[b] fluorescent rate constant $k_f = \varphi_F/\tau$;
[c] non-fluorescent rate constant $k_{nf} = 1/\tau - k_f$.

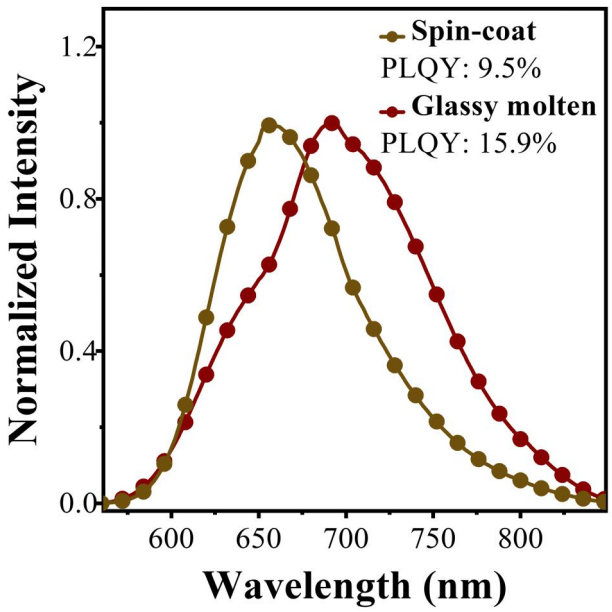


Fig. S9 PL spectra of **MPBM** in spin-coat film and molten film states.

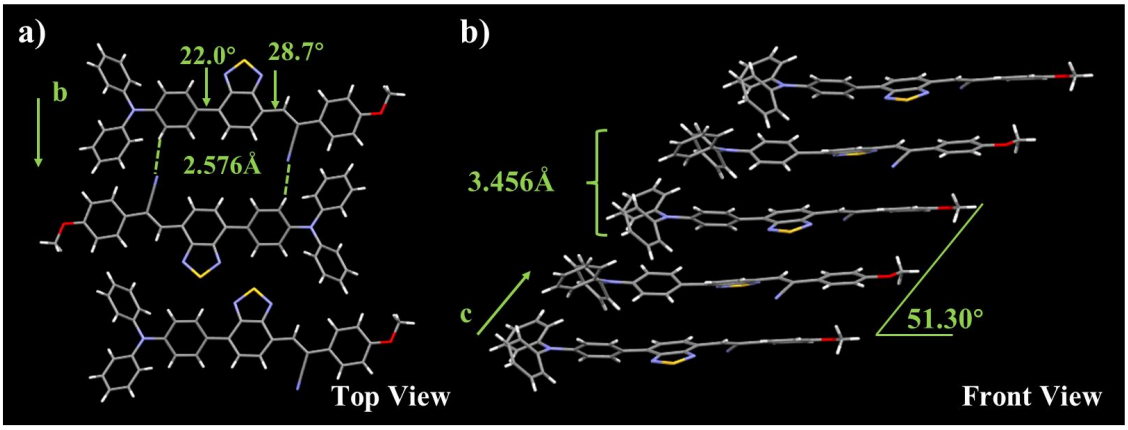


Fig. S10 Crystal structures of **MPBM**: a) the torsion angles and the illustration of C–H•••N hydrogen bond interactions of the **MPBM** in the crystalline state and b) the front view of the parallel arrangement.

Table S3 Crystal data and structure refinement for **Crystal-a, Crystal-b**, and **MPBM**.

Samples	**Crystal-a (CCDC: 2222362)**	**Crystal-b (CCDC: 2222364)**	**MPBM (CCDC:2225943)**
Formula	C51H41N5S	C51H41N5S	C34H24N4OS
Mr	771.95	771.95	536.63
Temperature(K)	272	271	273
Crystal system	monoclinic	triclinic	monoclinic
Space group	Cc	P-1	P 21/c
a(Å)	37.963(10)	10.2793(16)	17.498(11)
b(Å)	11.197(3)	13.021(4)	15.363(7)
c(Å)	19.378(2)	17.825(5)	10.416(3)
α(°)	90	102.094(13)	90
β(°)	100.514(12)	99.856(13)	106.58(3)
γ(°)	90	105.936(12)	90
V(Å^3)	8099(3)	2716.1(10)	2684(2)
Z	8	2	4
D_{calc} (g/cm^3)	1.266	1.178	1.328
Theta Range(°)	2.367 – 68.501	2.613 – 68.379	2.635-68.447
F(000)	3248.0	812.0	1120
h, k, l_{max}	45, 13, 22	12, 15, 21	21, 18, 12
N_{ref}	12544	27454	4870
T_{min}, T_{max}	0.571, 0.753	0.647, 0.753	0.554, 0.753
Independent reflections	12544	7983	4870
Goodness-of-fit on F_2	1.001	1.016	1.049
R_{int}	0.0767	0.0618	0.1001
$R_1[I>2\sigma(I)]$	0.0520	0.0612	0.084
$wR_2[I>2\sigma(I)]$	0.1223	0.1542	0.2332
R_1(all data)	0.0815	0.1103	0.1464
wR_2(all data)	0.1535	0.1855	0.2741
S	1.001	1.016	1.049

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

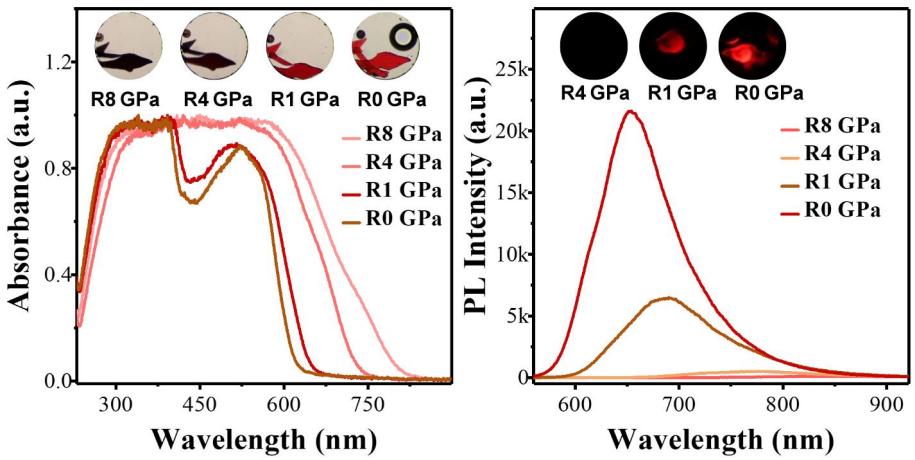


Fig. S11 a) *In situ* absorption spectra and b) PL spectra of **Crystal-a** during the depressurizing process. The inset images show normal and fluorescent photographs respectively under different pressures.

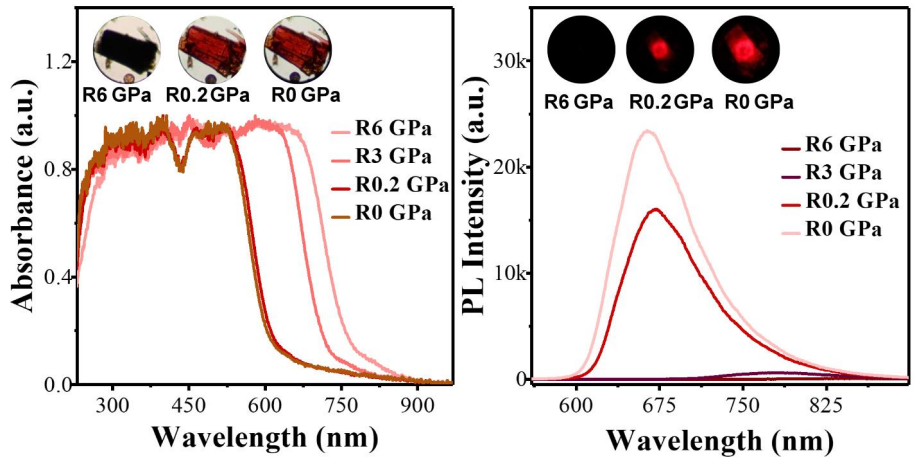


Fig. S12 a) *In situ* absorption spectra and b) PL spectra of **Crystal-b** during the depressurizing process. The inset images show normal and fluorescent photographs respectively under different pressures.

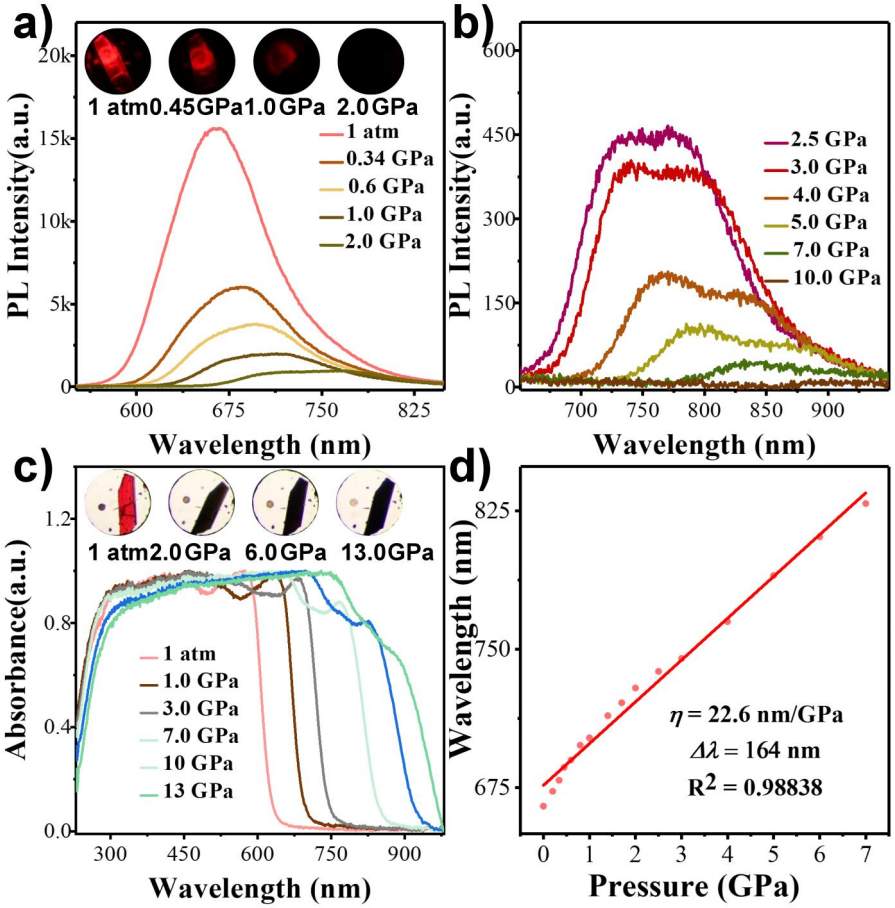


Fig. S13 a, b) *In situ* PL spectra and c) absorption spectra of **MPBM** under different hydrostatic pressures; d) The corresponding plots of the hydrostatic pressure versus PL peaks wavelength. The inset images of a, c) show the fluorescent and normal photographs respectively under different pressures.

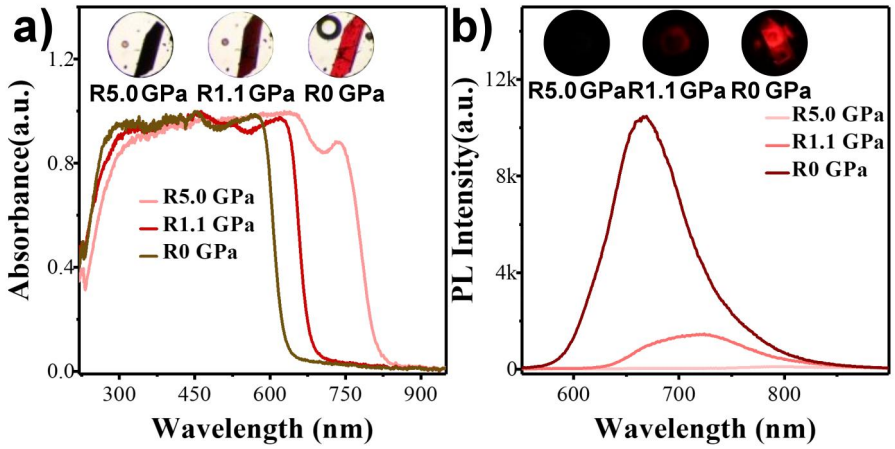


Fig. S14 a) *In situ* absorption spectra and b) PL spectra of **MPBM** during the

depressurizing process. The inset images show the normal and fluorescent photographs respectively under different pressures.

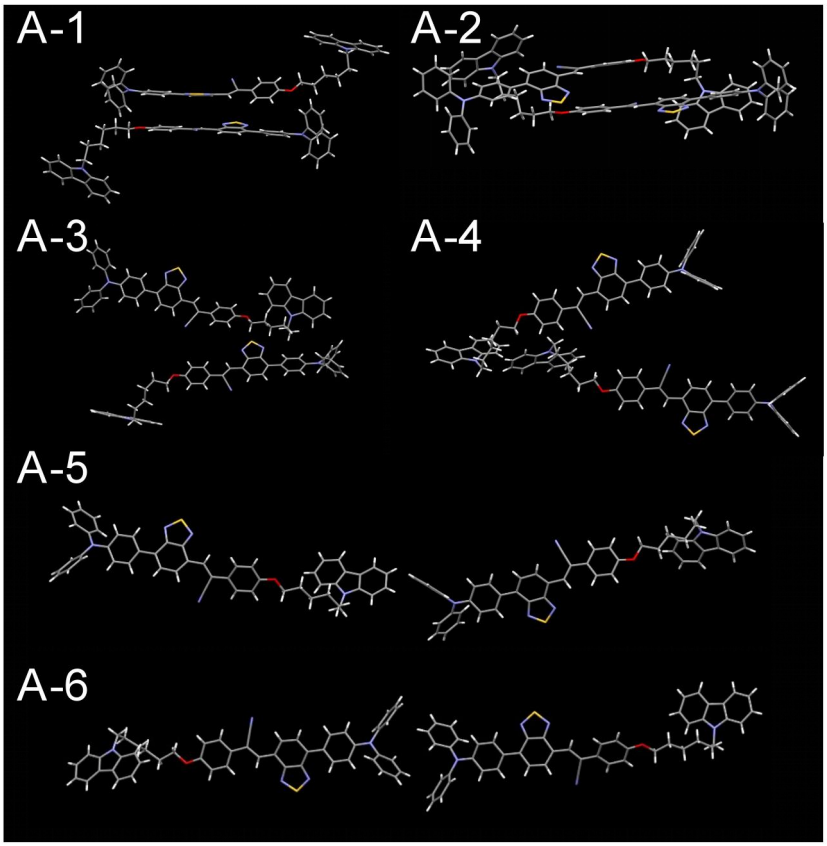


Fig. S15 Interacting dimers may be present in the Crystals-a.

Table S4 DFT at the B3LYP/6-31G (d, p) level calculations of excited states of dimers and monomer in Crystals-a.

	Energy[a] (eV)	Wavelength (nm)	*f* [b]
A-1	1.945	637.47	0.0654
A-2	2.0337	609.65	1.1029
A-3	2.0323	610.06	0.0005
A-4	2.1008	590.16	0.3738
A-5	2.1306	581.92	1.2833
A-6	2.1166	585.76	1.6625
monomer	2.1342	580.94	0.6958

[a] excitation energies for different configurations;
[b] *f* is oscillator strength.

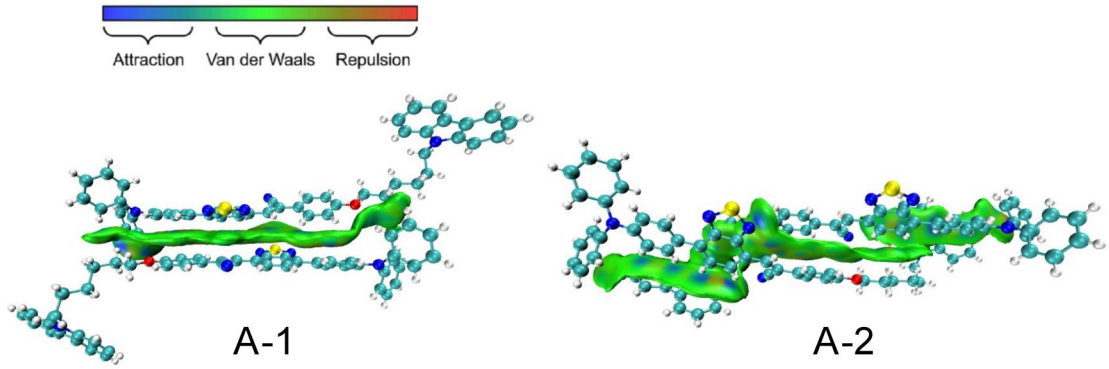


Fig. S16 Visualization of intermolecular interactions for A-1and A-2 phases, respectively, predicted by the IGM method.

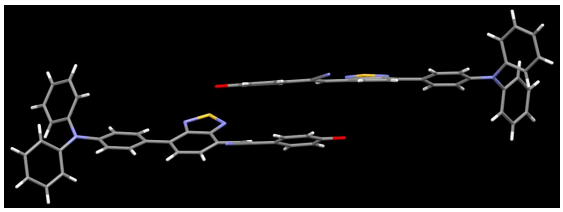


Fig. S17 A-X dimer from A-2 dimer by cut-off alkyl carbazole.

Table S5 Interaction energy decomposition of the A-1, A-2 and A-X dimers, respectively, calculated based on the EDA method, where energies are in kJ/mol.

	Electrostaic	Repulsion	Dispersion	Total
A-1	-1.31	72.05	-192.40	-121.66
A-2	-23.65	74.37	-221.64	-170.92
A-X	-4.67	42.67	-104.87	-66.97

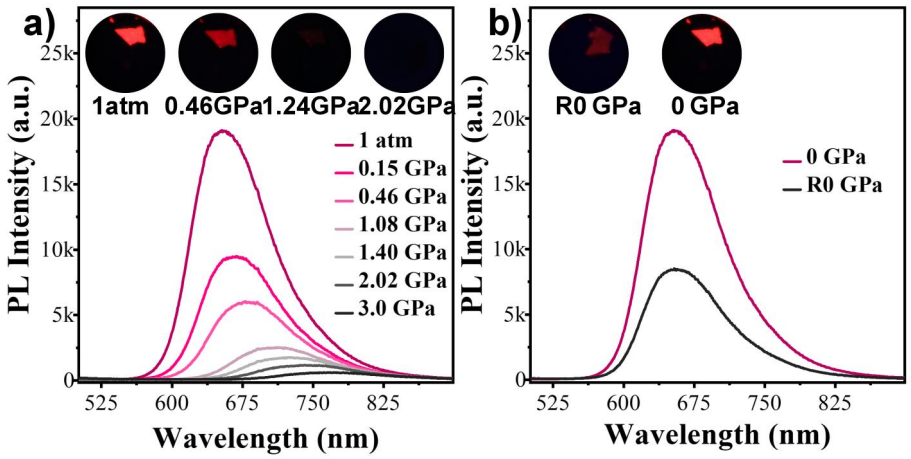


Fig. S18 a, b) *In situ* PL spectra of **MPBM-Cz3** under different hydrostatic pressures. R for release pressure.

References

[1] Q. Luo, L. Li, H. Ma, C. Lv, X. Jiang, X. Gu, Z. An, Z. Bo, C. Zhang and Y. Zhang, *Chem. Sci.* 2020, **11**, 6020-6025.

[2] J. Sun, S. Yang, J. Wu, X. He, Y. Zhang, J. Ji, C. Zhang and Z. Liang, *Chem. Eng. J.* 2022, **428**, 132625.