

Supporting Information

Designing Organic Room Temperature Phosphorescence with Ultralong Lifetime by Substituent Modification

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Experimental Section

Materials and instruments. 9H-carbazole, methyl 4-bromobenzoate, potassium carbonate, Pd(t-Bu₃P)₂, are purchased from Alfa Aesar Co. and use without further purification. The solvents for synthesis are common commercial grade. ¹H NMR and ¹³C NMR spectra are recorded on a Bruker 400 (400 MHz) spectrometer. Fluorescence spectroscopic studies are performed on a fluorescence spectrophotometer (Horiba Jobin Yvon FluoroMax-4 NIR, NJ, USA). UV-vis spectra are obtained on a spectrometer (Cintra 20, GBC, Australia). The percentage distribution of each lifetime component to the total decay curve and photoluminescence quantum yield is recorded using an Edinburgh Instruments FLS-980 and FS-5 fluorospectrophotometer. Powder X-ray diffraction (PXRD) patterns carried by a D/max2500 VB2+/PC X-ray diffractometer (Rigaku) using Cu K α radiation in the 2 θ range 5-40°. Single crystals of CBM-CH₃ and CBM-OCH₃ were performed at 104 K with a Rigaku X-ray diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystallographic information has been deposited with Cambridge Crystallographic Data Centre and signed to CCDC code 1820457 for CBM, 2077531 for CBM-CH₃, 2077532 for CBM-OCH₃. The photos are taken by Canon 600D. High performance liquid chromatography

(HPLC) was performed on an Agilent 1260 Infinite HPLC system using a Agilent 5 Prep-C18 column. The running rate was 0.8 mL/min, and running buffer was 100% THF.

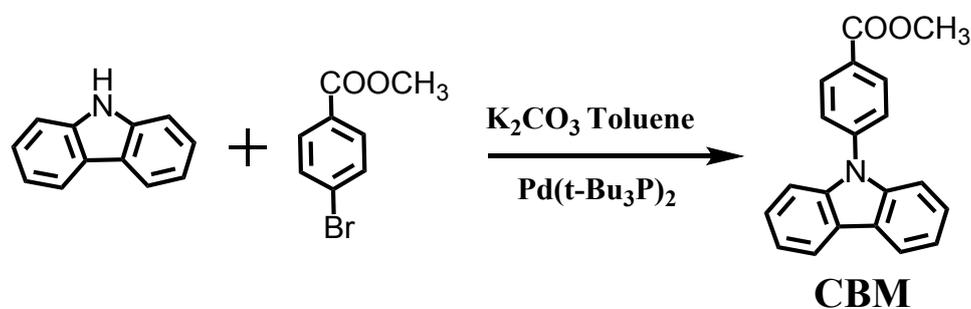
Computational methods

TD-DFT calculations were conducted on Gaussian 09 program. Ground state (S_0) geometries of these compounds were directly selected from single crystal structures and were used as molecular models without further optimization. On the basis of this, exciton energies in singlet (S_n) and triplet states (T_n) were estimated through a TD-DFT method at the TD-B3LYP/6-31+G (d, p) level.^[1] Kohn-Sham frontier orbital analysis was subsequently performed based on the results of theoretical calculation to elucidate the mechanisms of possible singlet-triplet intersystem crossings, in which the channels from S_1 to T_n are believed to share part of the same transition orbital compositions.^[2] All the natural transition orbitals (NTO) analysis were evaluated by Multiwfn program based on TD-DFT results using Gaussian 09 package.^[3] Spin-orbital coupling matrix elements were investigated by ORCA program (version 4.1) based on the TD-DFT results.^[4-6] The fraction free volume was calculated through Materials Studio software (version 7.0) from Accelrys Inc.^[7] All the molecular models are selected from the single crystal structures.

Synthesis and characterizations

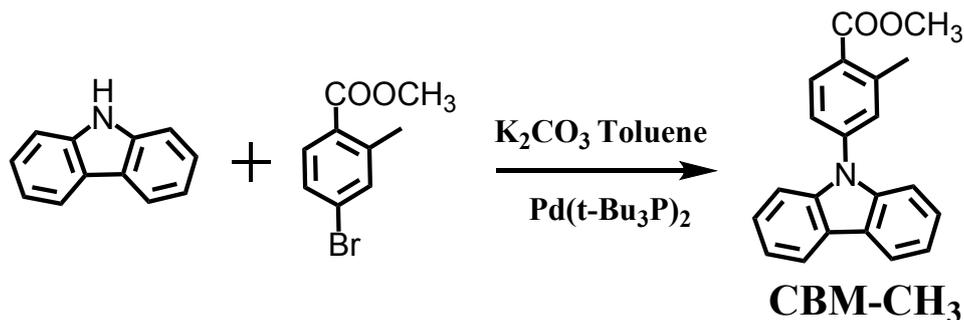
Synthesis of CBM: Under nitrogen atmosphere, 9H-carbazole (501 mg), methyl 4-bromobenzoate (645 mg), Pd(*t*-Bu₃P)₂ (10 mg), potassium carbonate (500 mg) were suspend in toluene (10 mL). The toluene solution was allowed to reflux at 110°C for 12

h and then cooled to room temperature. After removing the solvent, the residue was dissolved in dichloromethane and then washed with water. The organic phase was dried over anhydrous Na_2SO_4 . The obtained crude product used column chromatography to provide a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.29 (d, $J = 8.4$ Hz, 2H), 8.15 (d, $J = 7.7$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.45 (dt, $J = 8.2, 7.7$ Hz, 4H), 7.32 (t, $J = 7.3$ Hz, 2H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.55 (s), 142.19 (s), 140.41 (s), 131.51 (s), 128.81 (s), 126.44 (d, $J = 23.4$ Hz), 123.94 (s), 120.63 (d, $J = 9.6$ Hz), 109.89 (s), 52.49 (s). ESI-TOF: $\text{C}_{20}\text{H}_{15}\text{NO}_2$, m/z calcd for $[\text{M}+\text{H}]^+$ 302.36, found, 312.1199.



Scheme S1. Synthesis route for CBM.

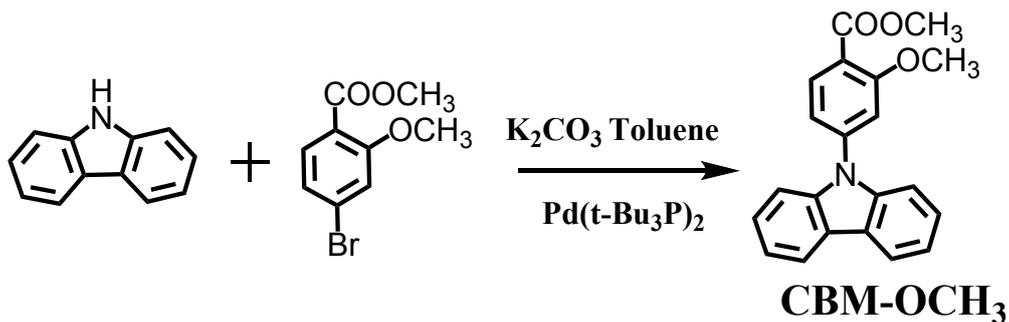
Synthesis of CBM- CH_3 : Under nitrogen atmosphere, 9H-carbazole (501 mg), methyl 4-bromo-2-methylbenzoate (687 mg), $\text{Pd}(\text{t-Bu}_3\text{P})_2$ (10 mg), potassium carbonate (500 mg) were suspended in toluene (10 mL). The toluene solution was allowed to reflux at 110°C for 12 h and then cooled to room temperature. After removing the solvent, the residue was dissolved in dichloromethane and then washed with water. The organic phase was dried over anhydrous Na_2SO_4 . The obtained crude product used column chromatography to provide a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (dd, $J = 10.3, 7.7$ Hz, 3H), 7.52 – 7.39 (m, 6H), 7.31 (d, $J = 14.6$ Hz, 2H), 3.97 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.51 (s), 142.70 (s), 141.10 (s), 140.48 (s), 132.59 (s), 129.60 (s), 128.28 (s), 126.25 (s), 123.88 (d, $J = 7.9$ Hz), 120.53 (d, $J = 2.1$ Hz), 109.97 (s), 52.17 (s), 22.11 (s). ESI-TOF: $\text{C}_{21}\text{H}_{17}\text{NO}_2$, m/z calcd for $[\text{M}+\text{H}]^+$ 316.35, found, 316.1347.



Scheme S2. Synthesis route for CBM-CH₃.

Synthesis of CBM-OCH₃:

Synthesis of CBM-OCH₃: Under nitrogen atmosphere, 9H-carbazole (501 mg), methyl 4-bromo-2-methoxybenzoate (703 mg), Pd(t-Bu₃P)₂ (10 mg), potassium carbonate (500 mg) were suspended in toluene (10 mL). The toluene solution was allowed to reflux at 110°C for 12 h and then cooled to room temperature. After removing the solvent, the residue was dissolved in dichloromethane and then washed with water. The organic phase was dried over anhydrous Na₂SO₄. The obtained crude product used column chromatography to provide a white powder. ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, J = 7.7 Hz, 2H), 8.06 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.46-7.41 (m, 2H), 7.34-7.30 (m, 2H), 7.25-7.20 (m, 2H), 3.97 (s, 3H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.19 (s), 160.60 (s), 142.70 (s), 140.43 (s), 133.38 (s), 126.35 (s), 123.87 (s), 120.61 (d, J = 3.1 Hz), 118.83 (s), 118.42 (s), 110.58 (s), 109.96 (s), 56.48 (s), 52.36 (s). ESI-TOF: C₂₁H₁₇NO₃, m/z calcd for [M+H]⁺ 332.36, found, 332.1308.



Scheme S3. Synthesis route for CBM-OCH₃ compounds.

Carbazole-based molecule structures reported with RTP properties

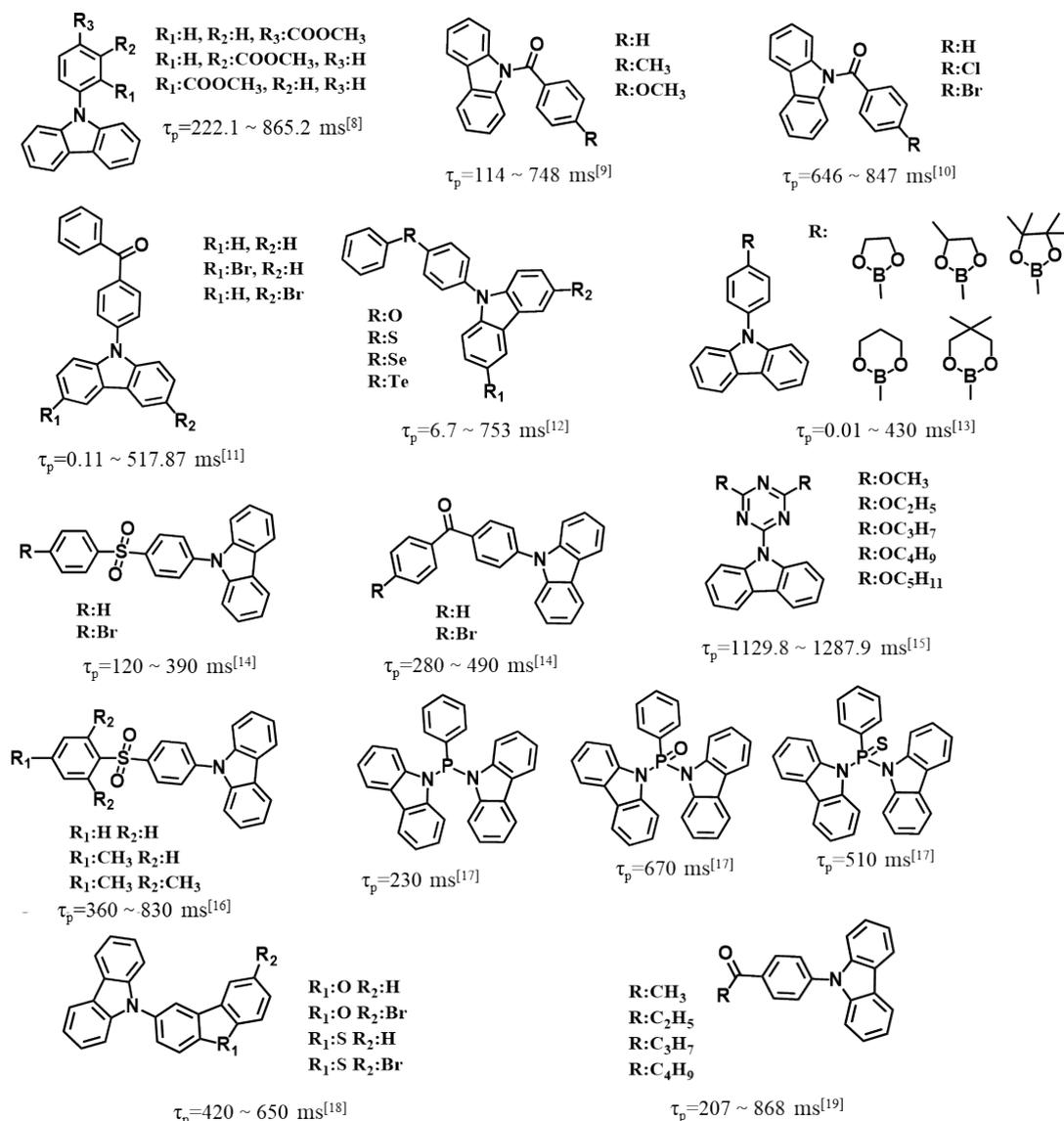


Fig. S1 Phosphorescence lifetime of the molecules reported with RTP properties.

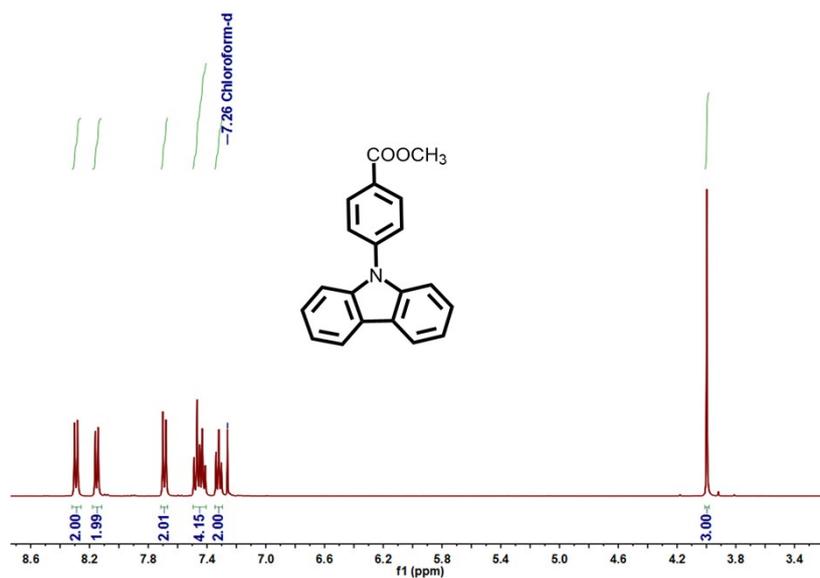


Fig. S2 ¹H NMR spectrum of CBM in CDCl₃.

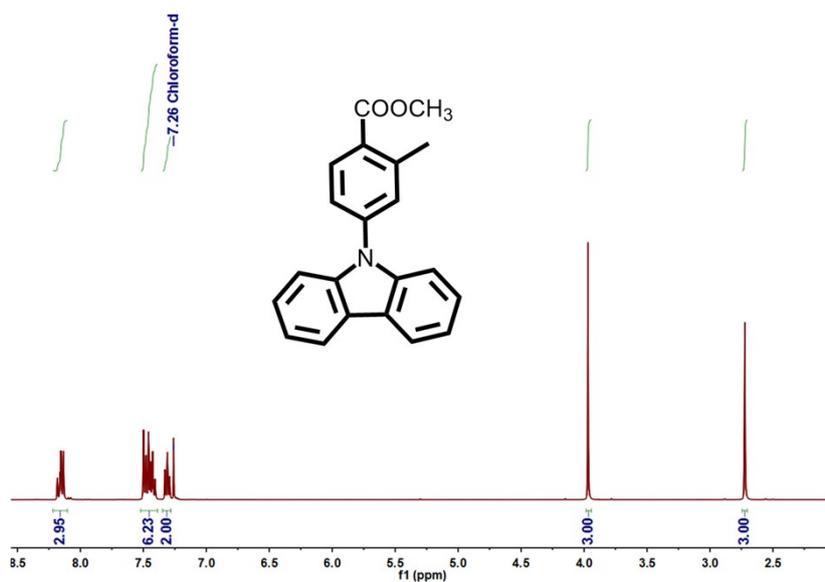


Fig. S3 ¹H NMR spectrum of CBM-CH₃ in CDCl₃.

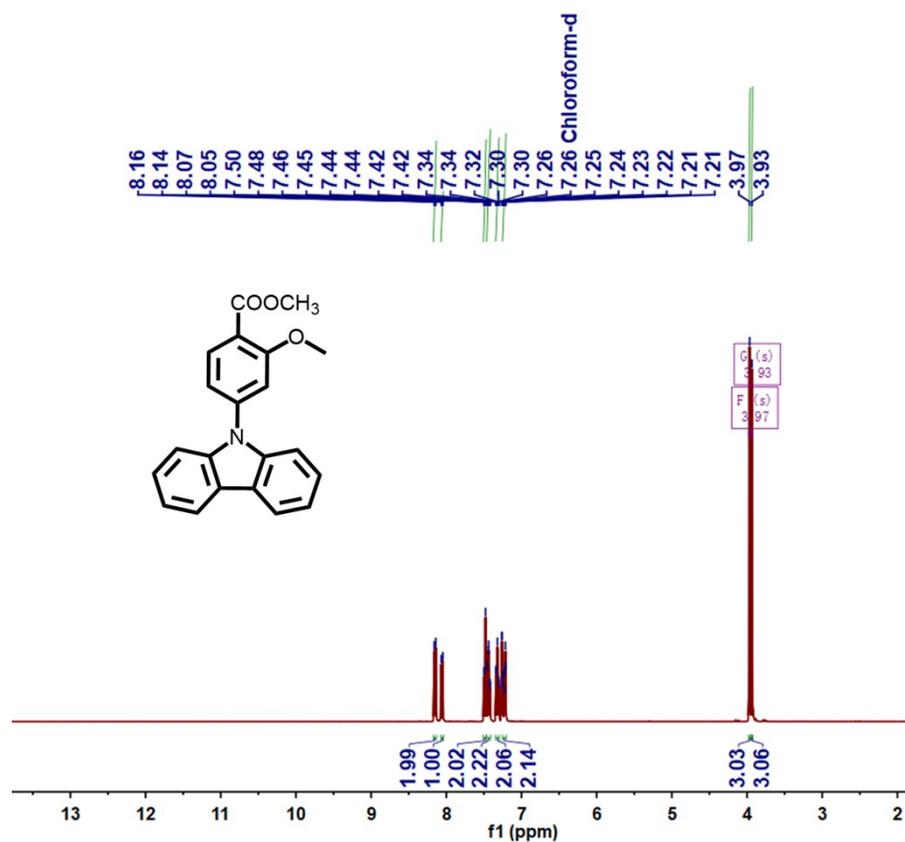


Fig. S4 ¹H NMR spectrum of CBM-OCH₃ in CDCl₃.

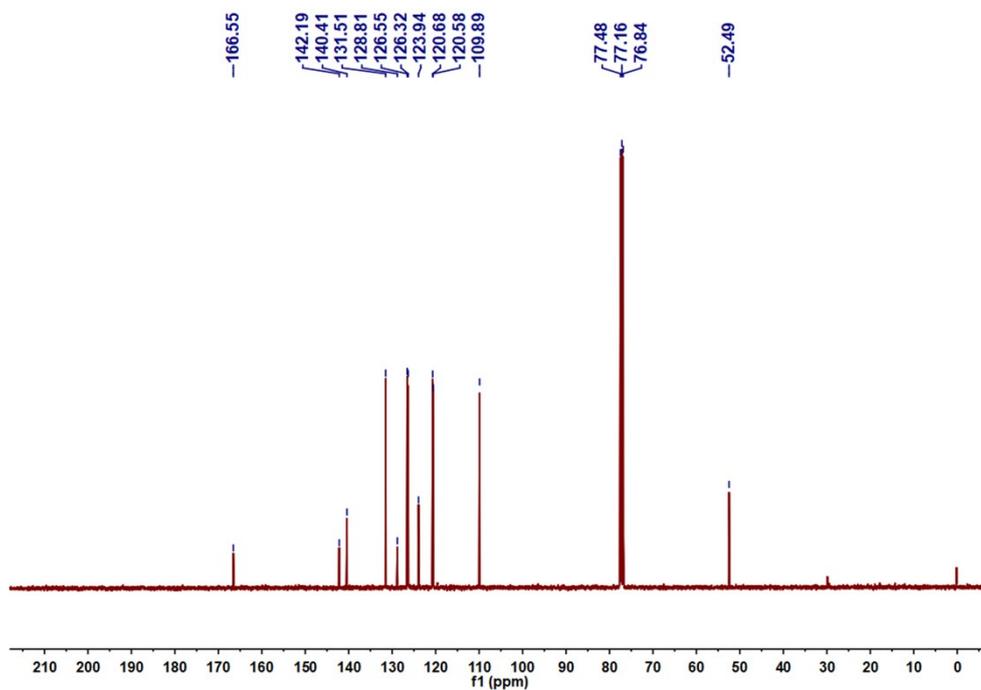


Fig. S5 ¹³C NMR spectrum of CBM in CDCl₃.

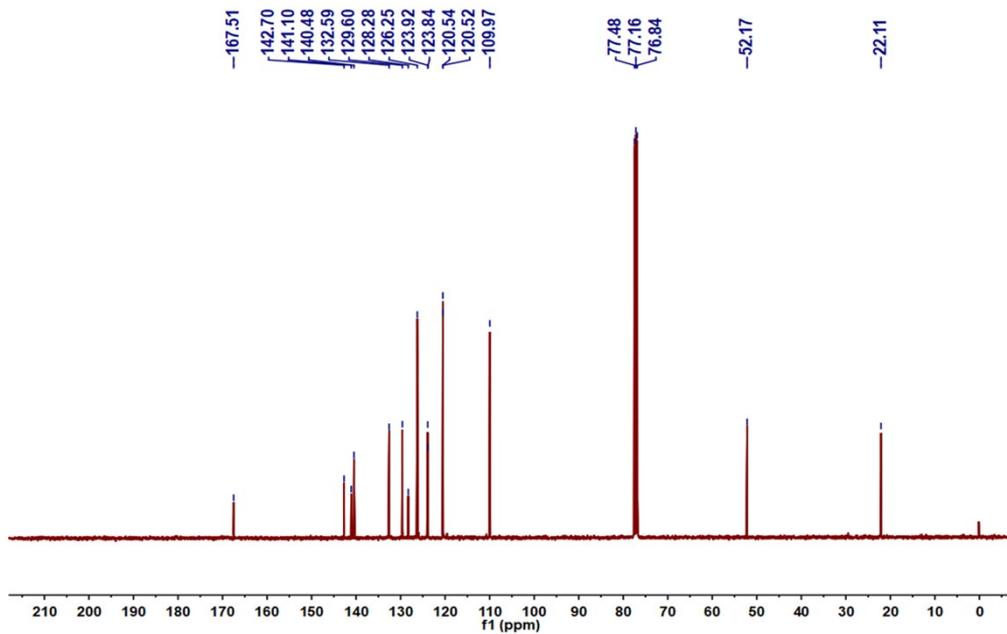


Fig. S6 ^{13}C NMR spectrum of CBM-CH₃ in CDCl₃.

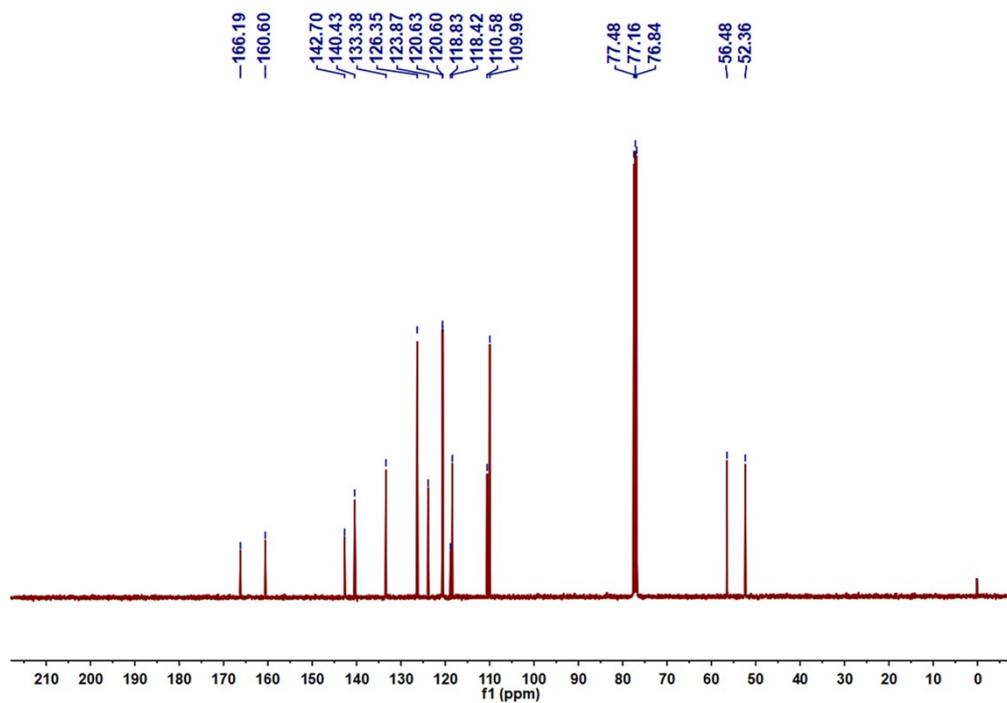


Fig. S7 ^{13}C NMR spectrum of CBM-OCH₃ in CDCl₃.

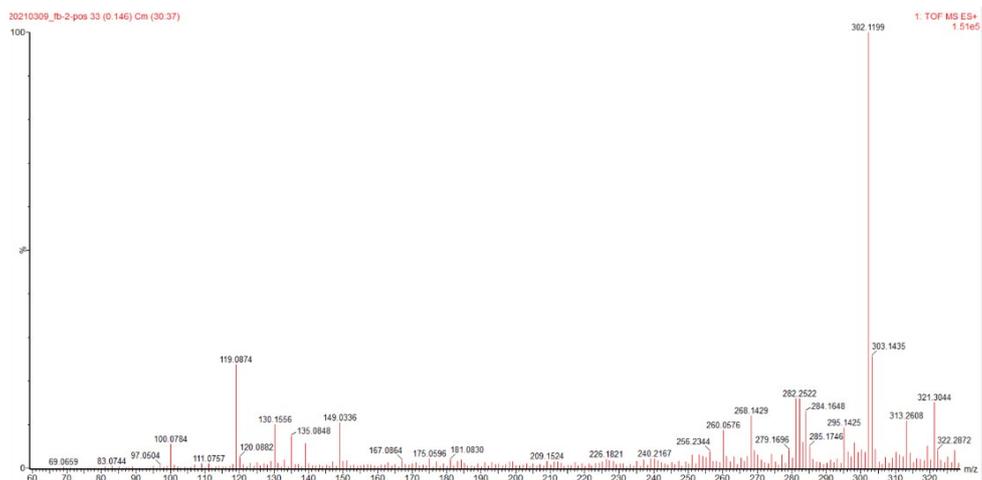


Fig. S8 ESI-TOF of CBM.

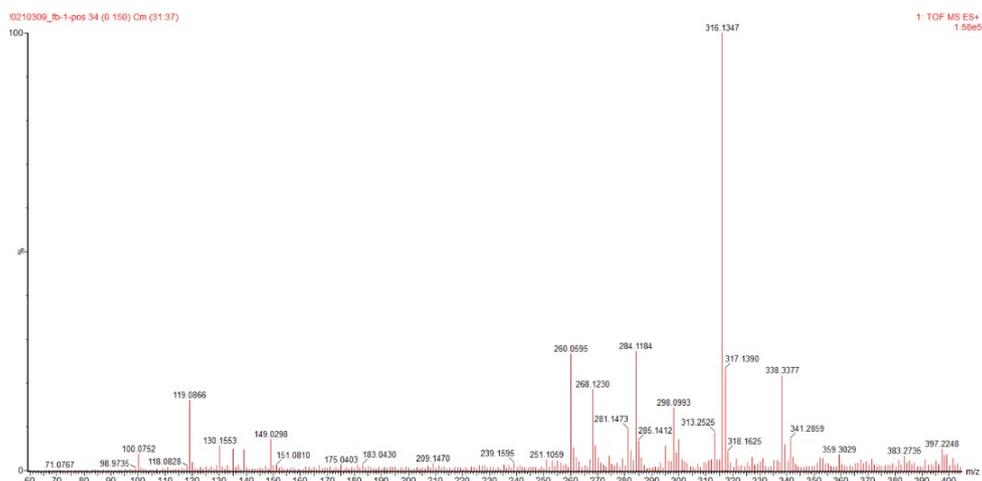


Fig. S9 ESI-TOF of CBM-CH₃.

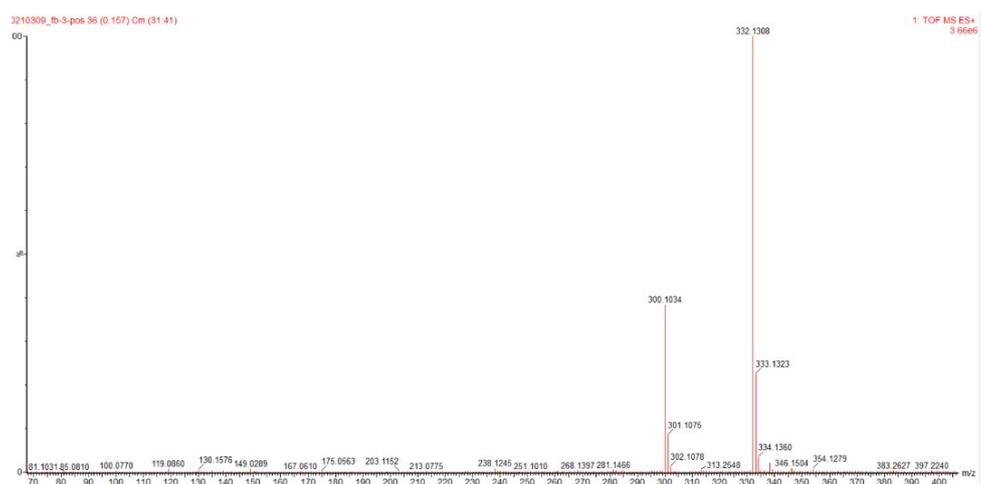


Fig. S10 ESI-TOF of CBM-OCH₃.

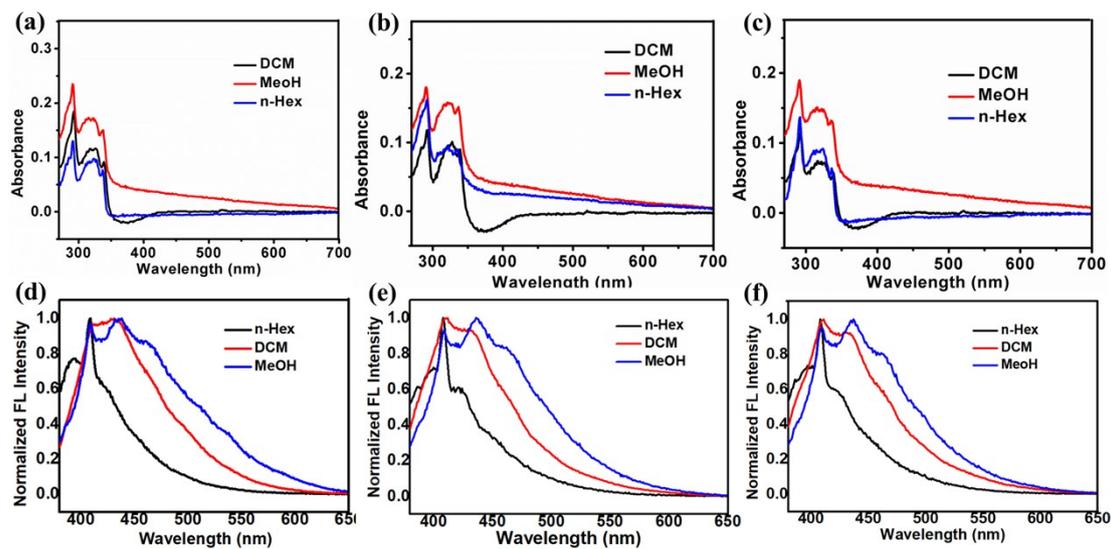


Fig. S11 (a) UV-vis absorption (10^{-5} M) and (b) Fluorescence (FL) spectra (10^{-5} M) of three carbazole-based compounds in DCM solution.

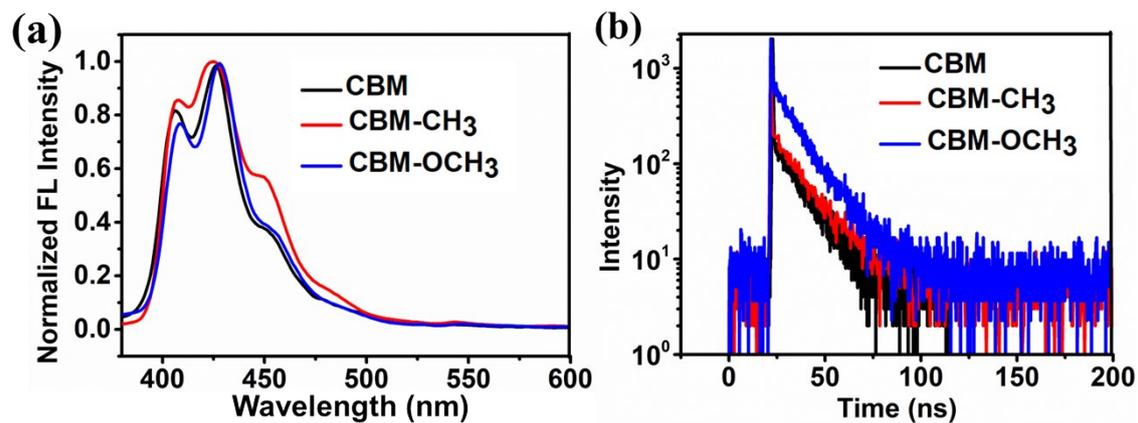


Fig. S12 (a) Normalized fluorescence (FL) spectra of three crystals excited by 365 nm. (b) Lifetime decay profiles of three crystals phosphorescence bands at 426 nm excited by 365 nm.

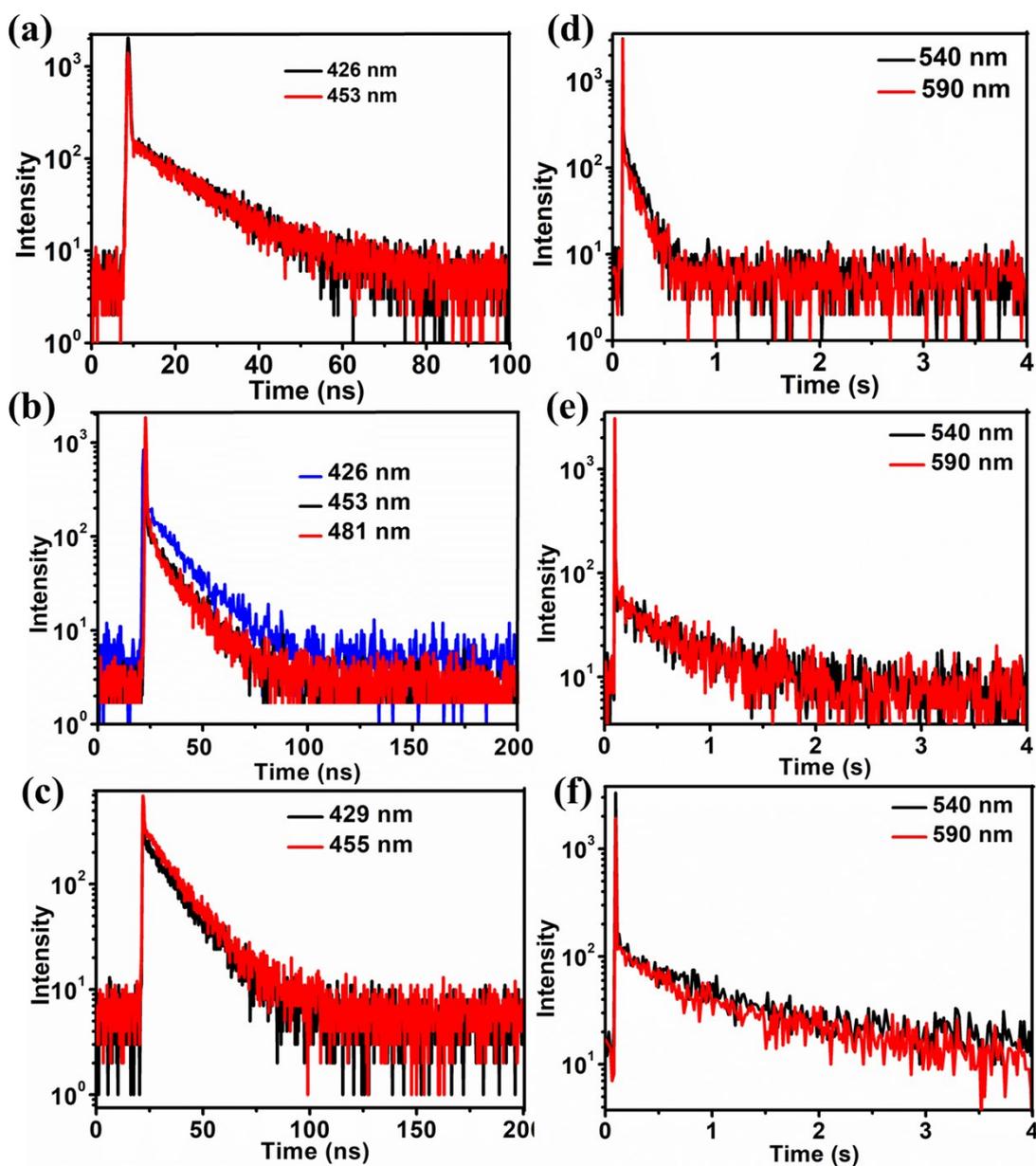


Fig. S13 Lifetime decay profiles of CBM (a, d), CBM-CH₃ (b, e) and CBM-OCH₃ (c, f) crystals fluorescence and phosphorescence bands excited by 365 nm.

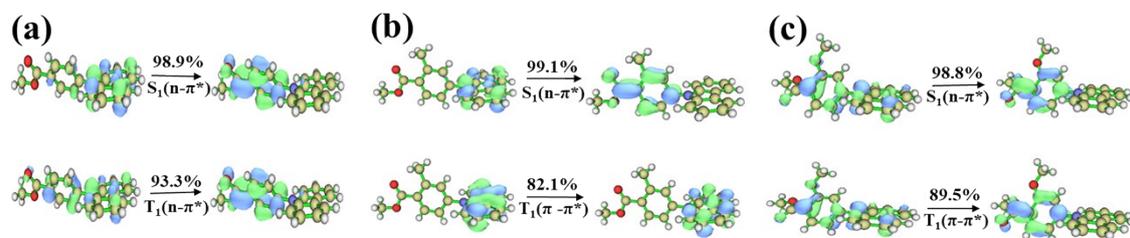


Fig. S14 Natural transition orbitals (NTOs) for S₁ and T₁ state of (a) CBM, (b) CBM-CH₃, (c) CBM-OCH₃.

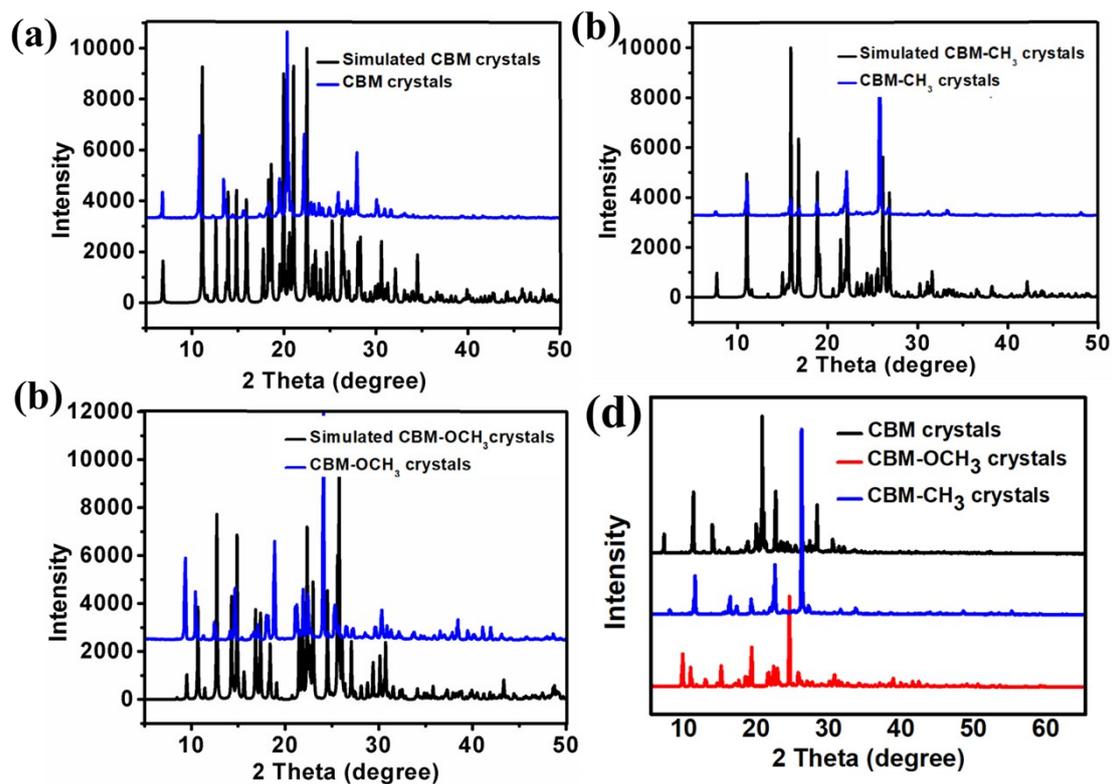


Fig. S15 Powder XRD pattern of three crystals and simulated pattern from their single crystal structures.

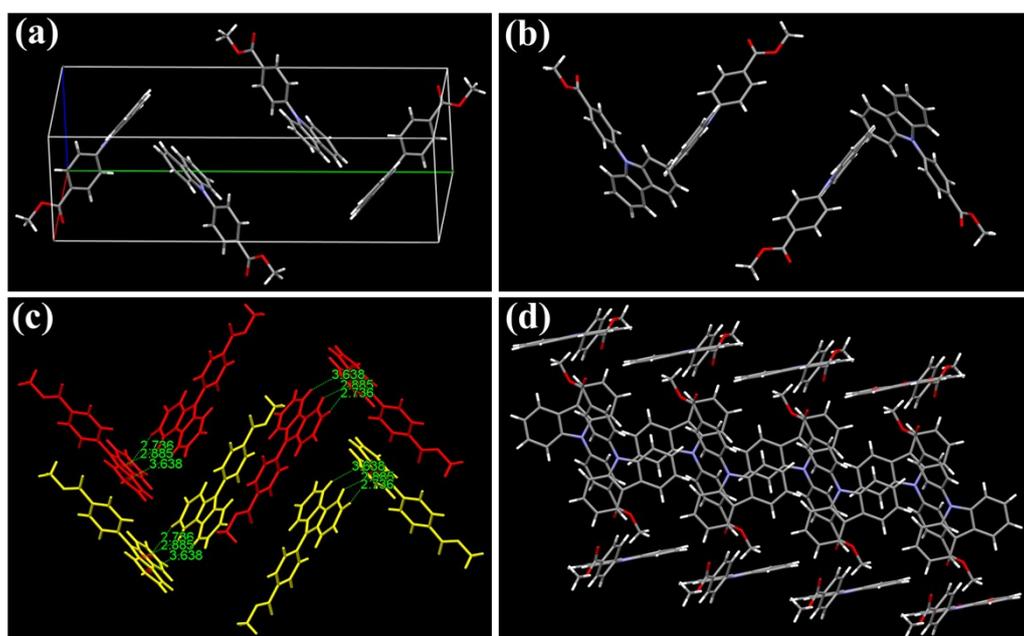


Fig. S16 Unit cell and intermolecular interactions of CBM with adjacent molecules.

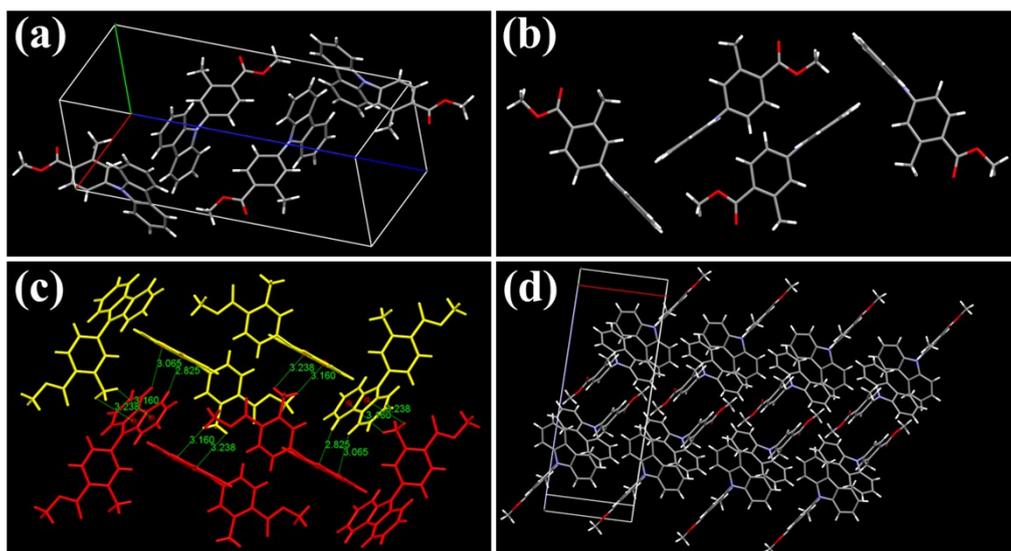


Fig. S17 Unit cell and intermolecular interactions of CBM-CH₃ with adjacent molecules.

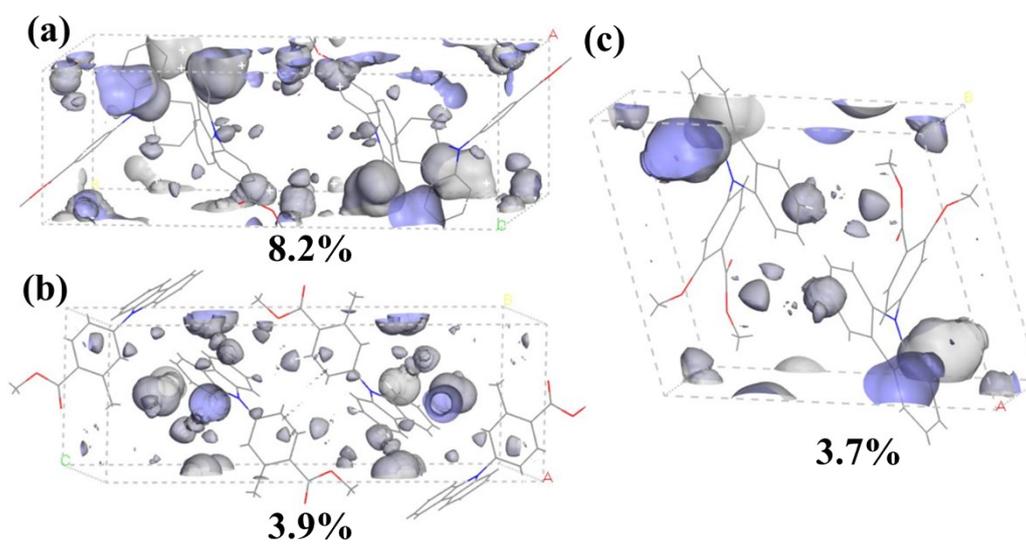


Fig. S18 Free volume region of (a) CBM, (b) CBM-CH₃, and (c) CBM-OCH₃ in single crystal cells.

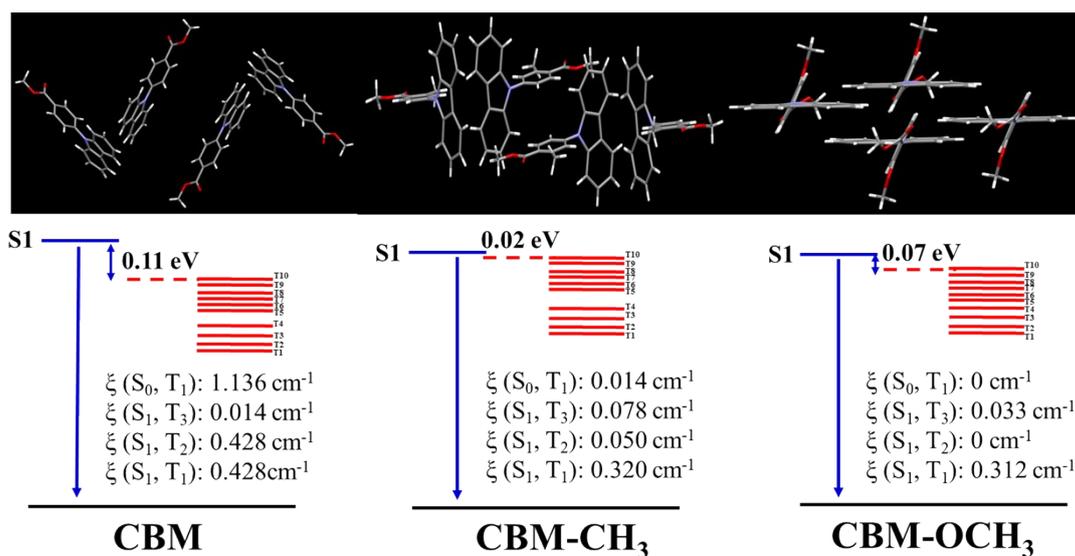


Fig. S19 Molecular packing structure, the energy level diagram and SOC value for CBM, CBM-CH₃ and CBM-OCH₃ crystals, respectively.

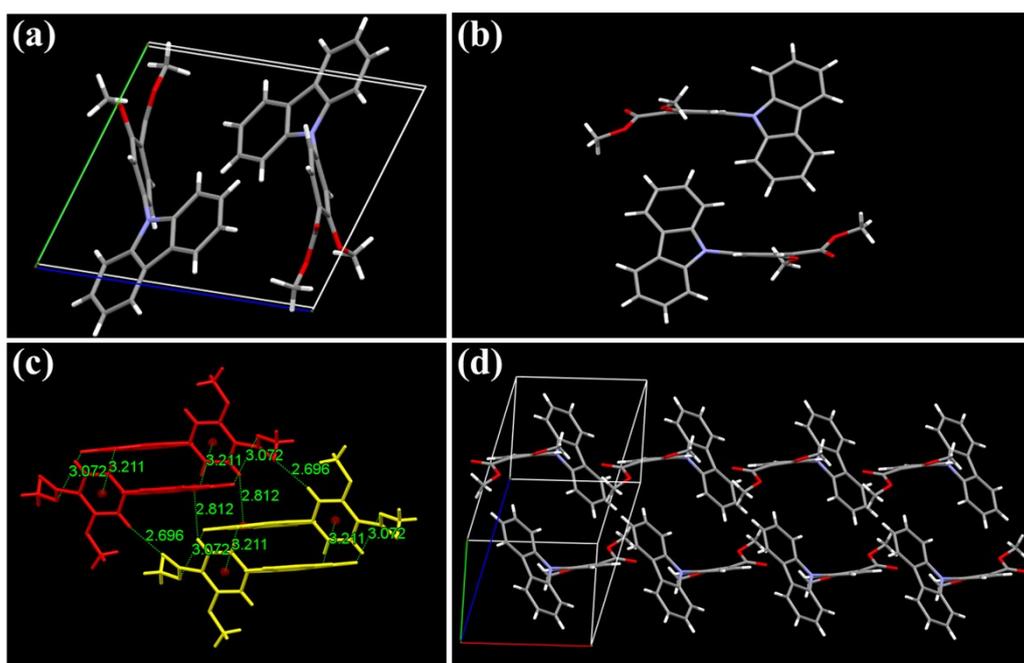


Fig. S20 Unit cell and intermolecular interactions of CBM-OCH₃ with adjacent molecules.

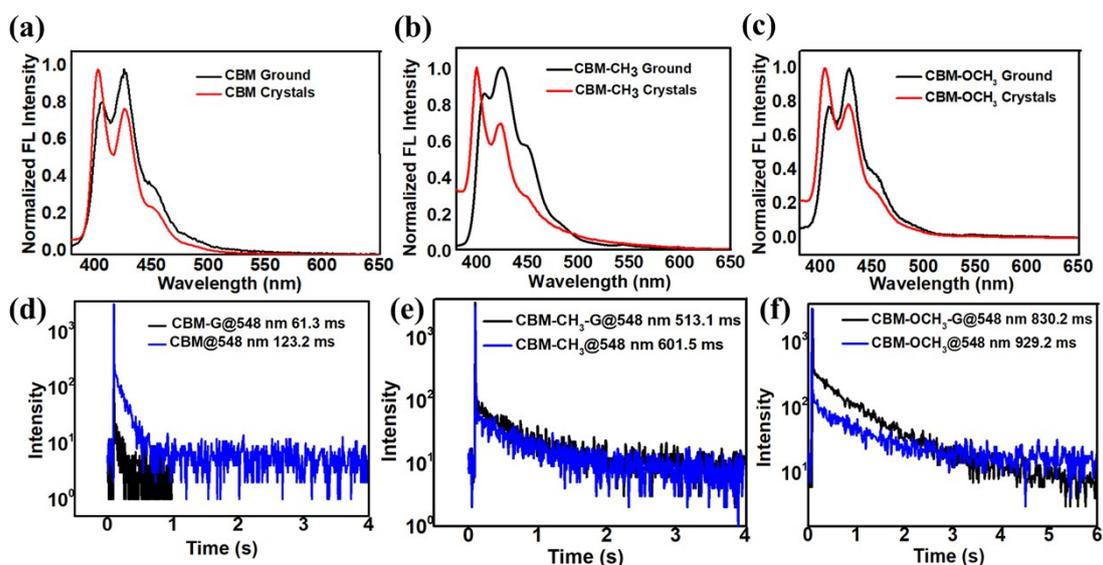


Fig. S21 Fluorescent spectra and phosphorescence bands at 548 nm lifetime decay profiles of three carbazole-based crystals before (a: CBM, b: CBM-CH₃, c: CBM-OCH₃) and after heavily ground (d: CBM-G, e: CBM-CH₃-G, f: CBM-OCH₃-G).

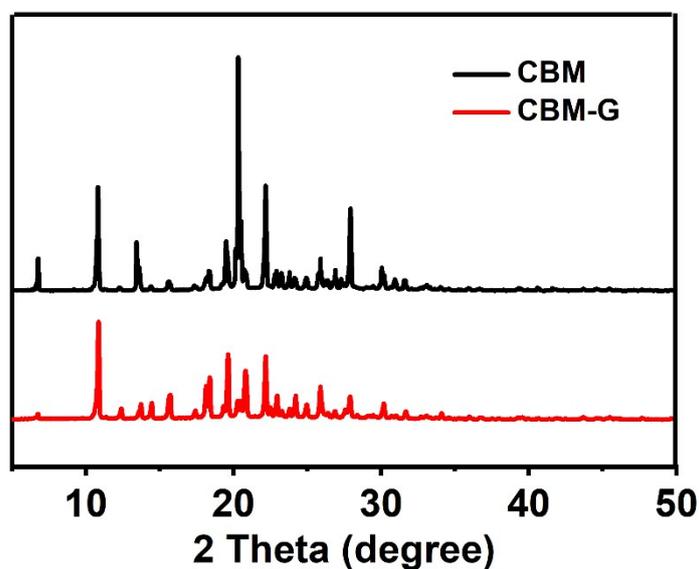


Fig. S22 XRD pattern of crystalline and ground samples of CBM.

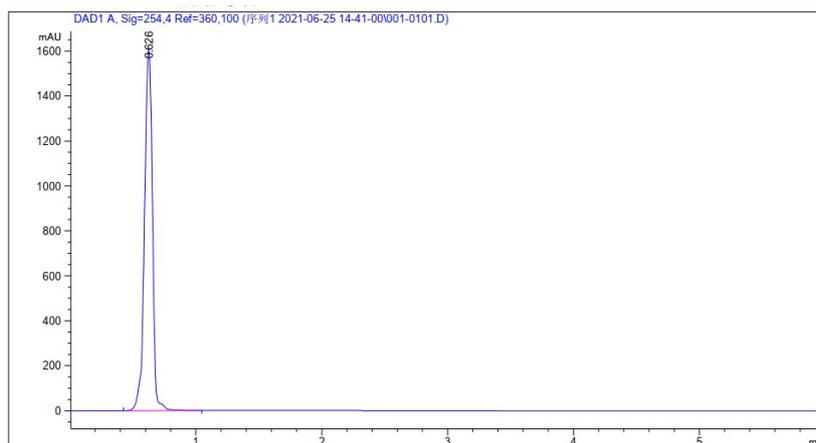


Fig. S23 High performance liquid chromatography diagrams of CBM.

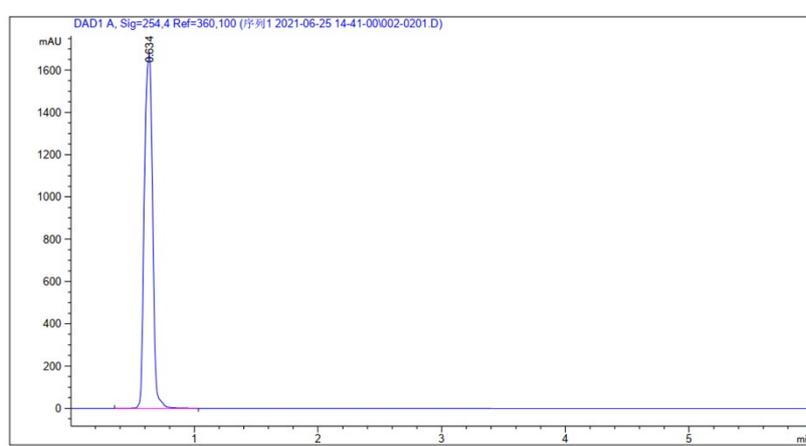


Fig. S24 High performance liquid chromatography diagrams of CBM-CH₃.

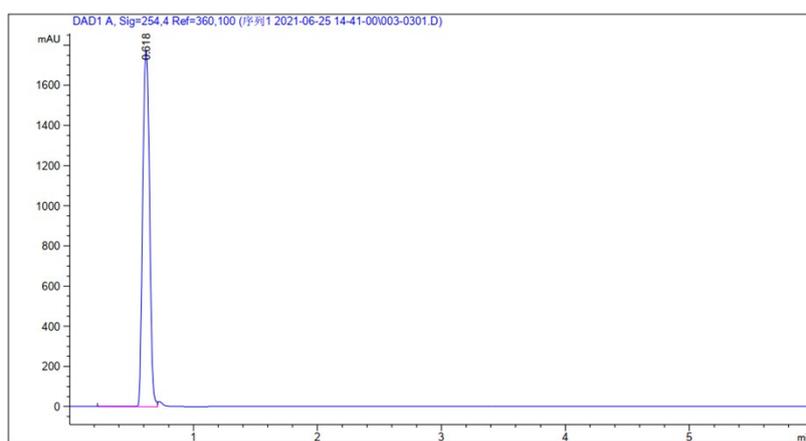


Fig. S25 High performance liquid chromatography diagrams of CBM-OCH₃.

Table S1. SOC matrix elements of CBM, CBM-CH₃ and CBM-OCH₃

SOC value	CBM (cm ⁻¹)	CBM-CH ₃ (cm ⁻¹)	CBM-OCH ₃ (cm ⁻¹)
$\xi(S_0, T_1)$	1.09	0.102	0.270
$\xi(S_1, T_1)$	0.188	1.119	0.231
$\xi(S_1, T_2)$	0.314	0.033	0.734
$\xi(S_1, T_3)$	0.606	0.330	0.333

Table S2. Crystal data for CBM, CBM-CH₃ and CBM-OCH₃.

Identification code	CBM	CBM-CH ₃	CBM-OCH ₃
Empirical formula	C ₂₀ H ₁₅ NO ₂	C ₂₁ H ₁₇ NO ₂	C ₂₁ H ₁₇ NO ₃
Formula weight	301.35	315.36	331.36
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2 ₁ /c	P2 ₁ /n	P-1
a / Å	8.1731(8)	8.6130(2)	7.9261(4)
b / Å	25.846(9)	8.1005(2)	9.7507(6)
c / Å	7.5022(17)	22.9376(6)	11.1901(5)
α / °	90	90	72.299(2)
β / °	103.436(2)	91.1990(10)	77.213(2)
γ / °	90	90	86.046(2)
Volume (Å ³)	1541.4(3)	1600.0(7)	803.45(7)
Z	4	4	2
$\rho_{\text{calc}} / \text{mg mm}^{-3}$	1.299	1.309	1.370
μ / mm^{-1}	0.084	0.084	0.092
F(000)	632	664	348

Reference

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