Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Manipulation of the Electronic and Structural Effects on the Solid-State Emission of Multiple Linked Anthracenyl-*o*-Carborane Dyads

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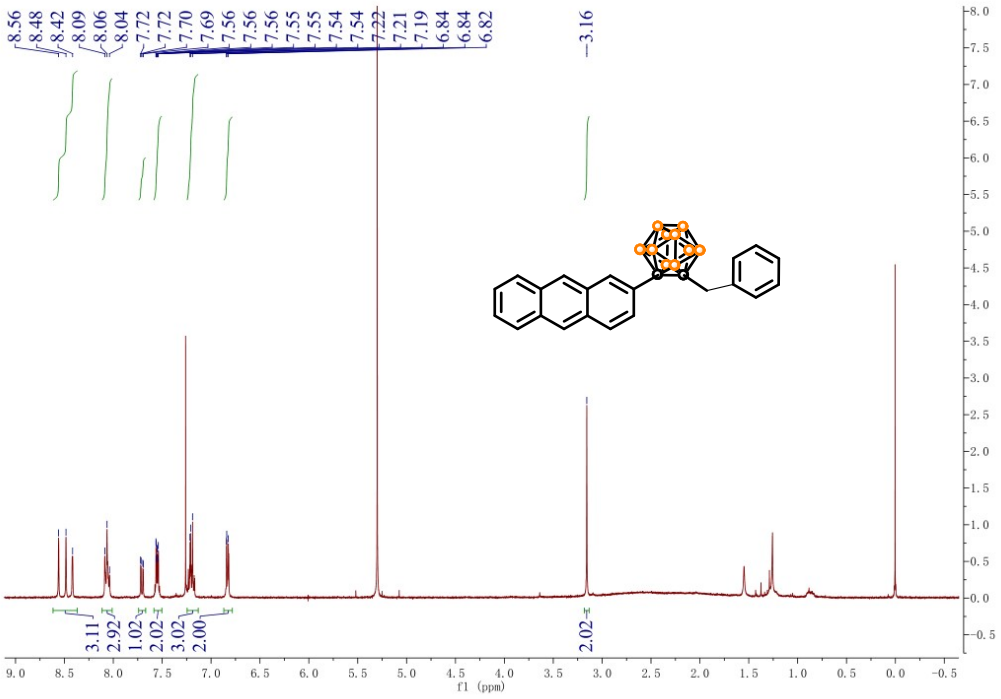

Figure S1. ^{1}H NMR spectroscopies of **CA1** in $CDCl_3$.

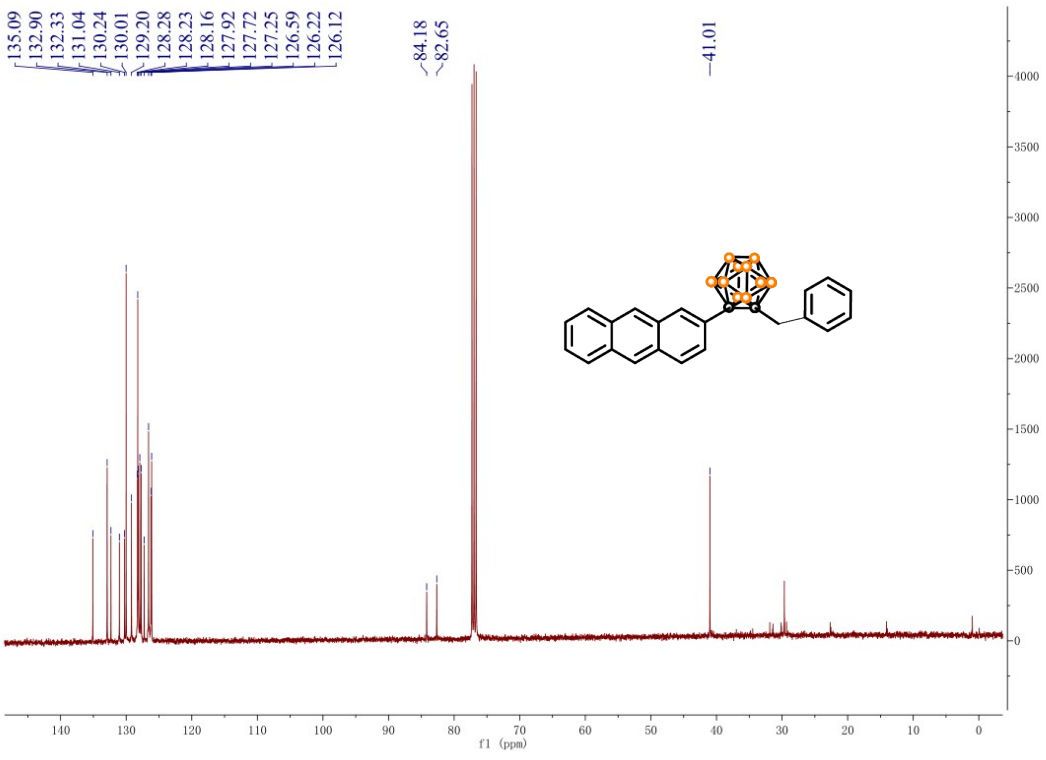

Figure S2. ^{13}C NMR spectroscopies of **CA1** in $CDCl_3$.

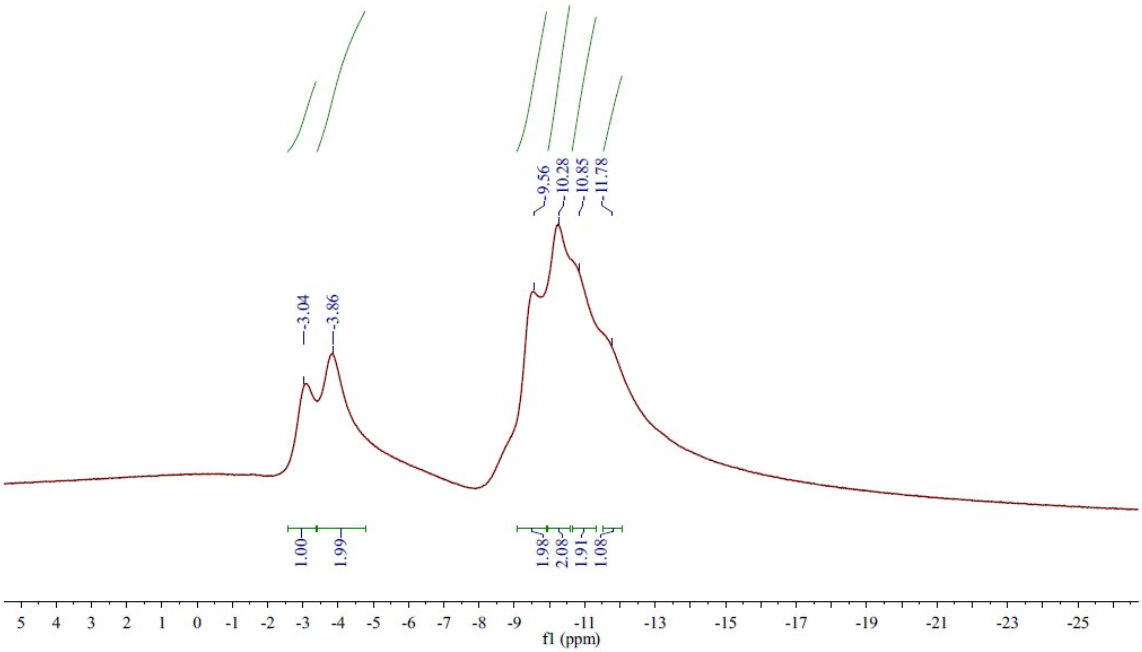

Figure S3. ^{11}B NMR spectroscopies of **CA1** in $CDCl_3$.

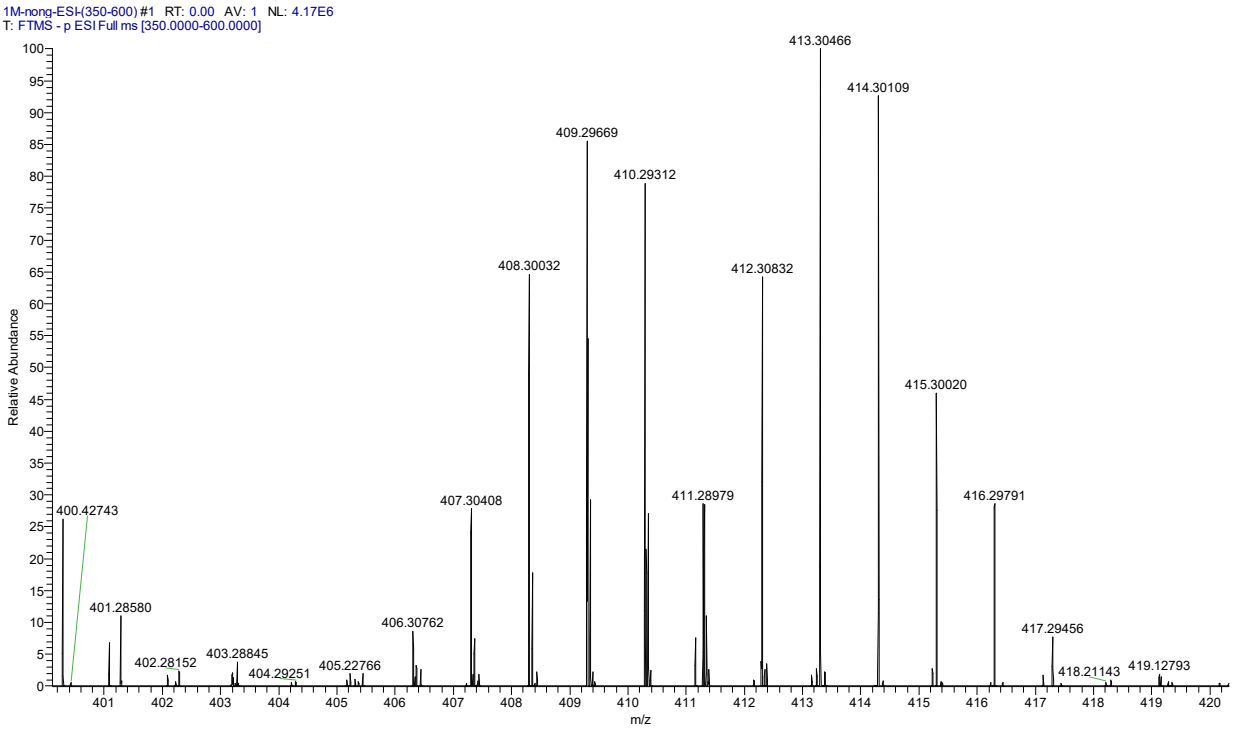

Figure S4. HRMS (ESI^-) spectrum of **CA1**.

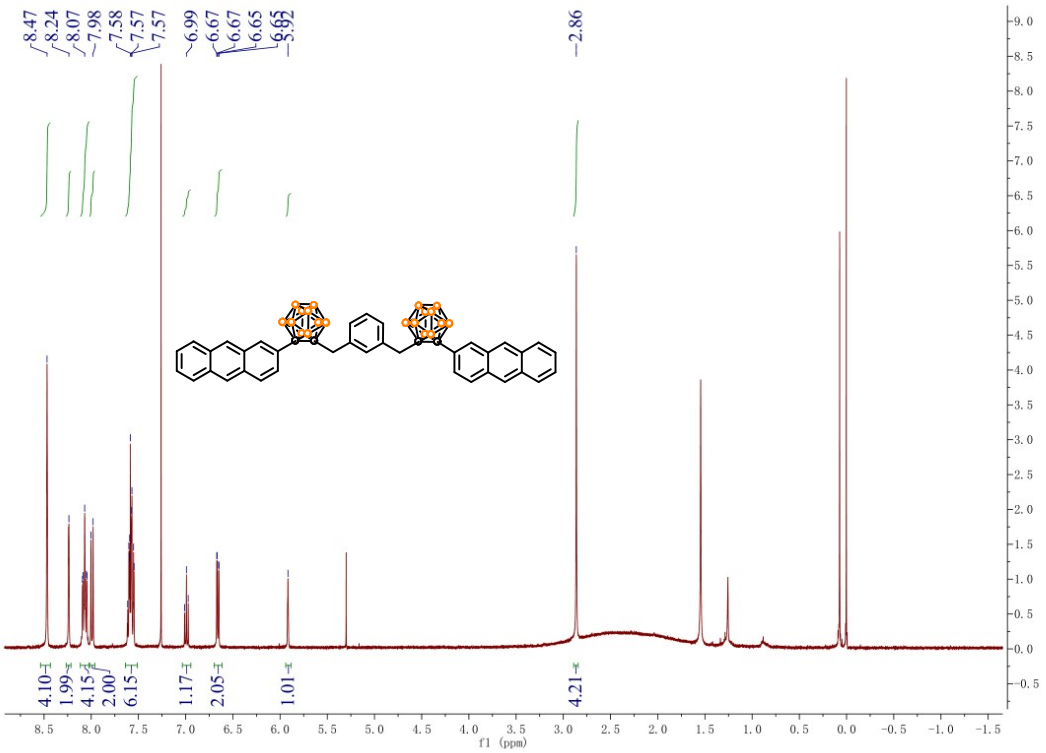

Figure S5. ^{1}H NMR spectroscopies of **CA2** in $CDCl_3$.

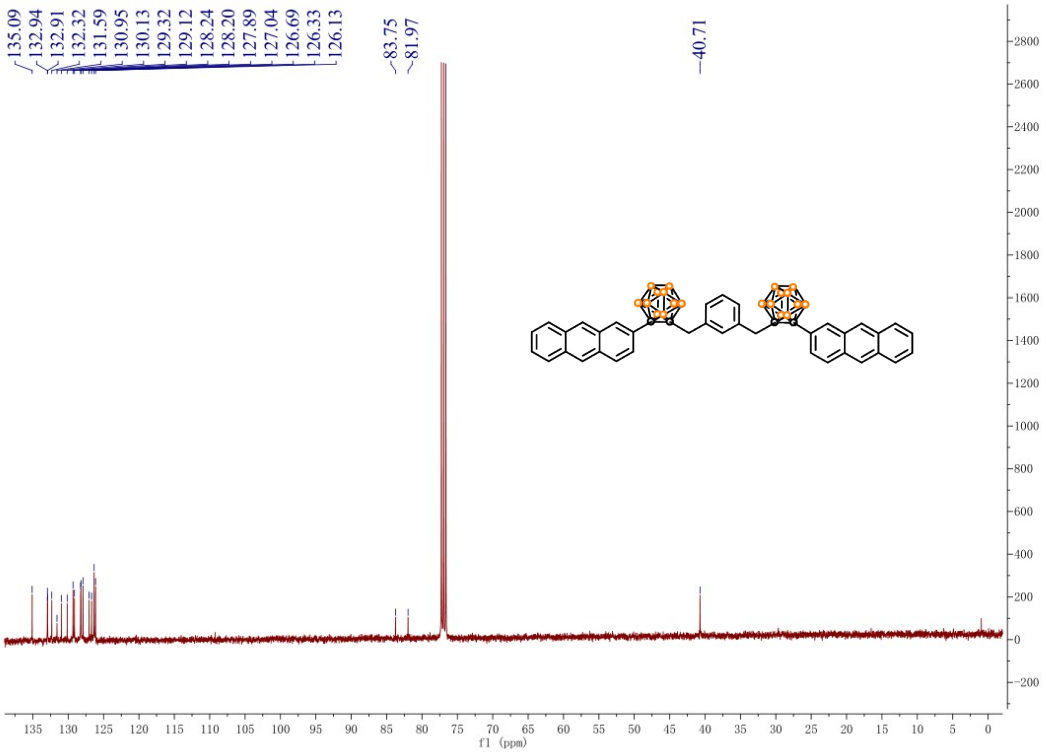

Figure S6. ^{13}C NMR spectroscopies of **CA2** in $CDCl_3$.

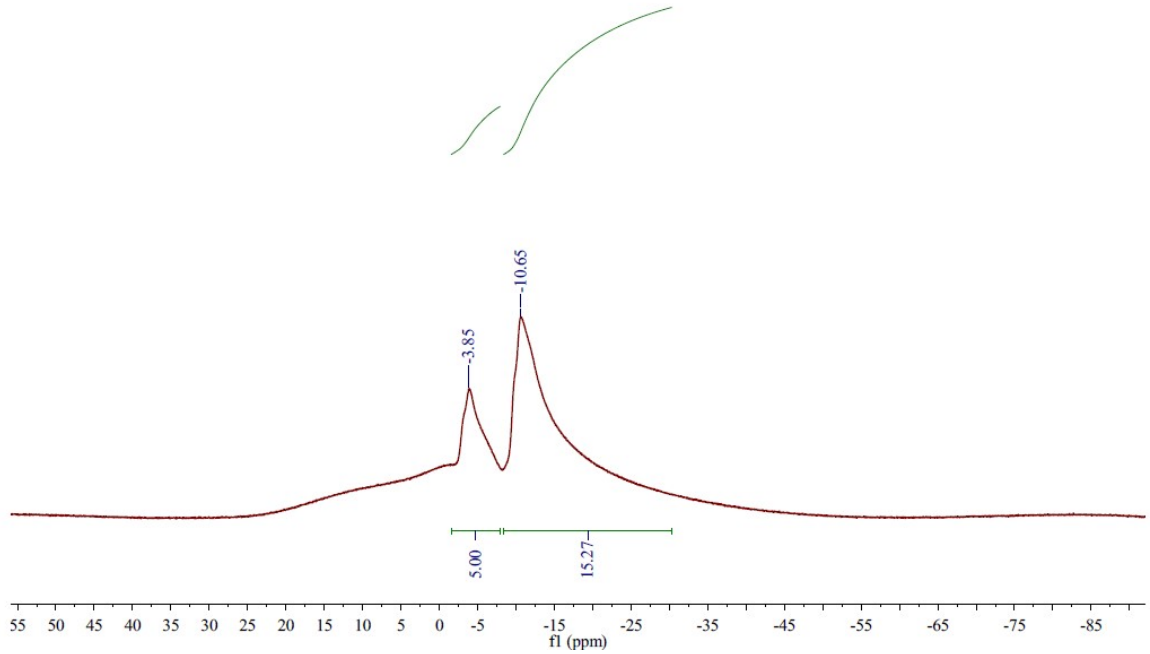

Figure S7. ^{11}B NMR spectroscopies of **CA2** in $CDCl_3$.

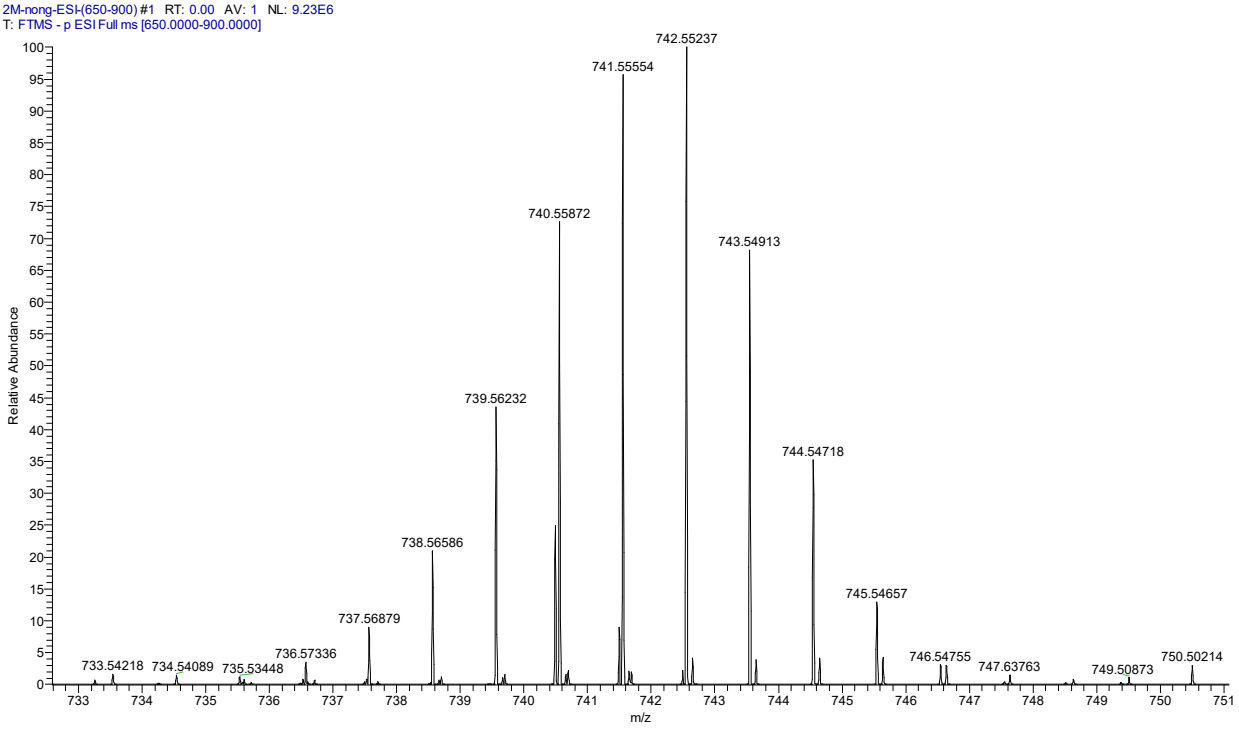

Figure S8. HRMS (ESI^-) spectrum of **CA2**.

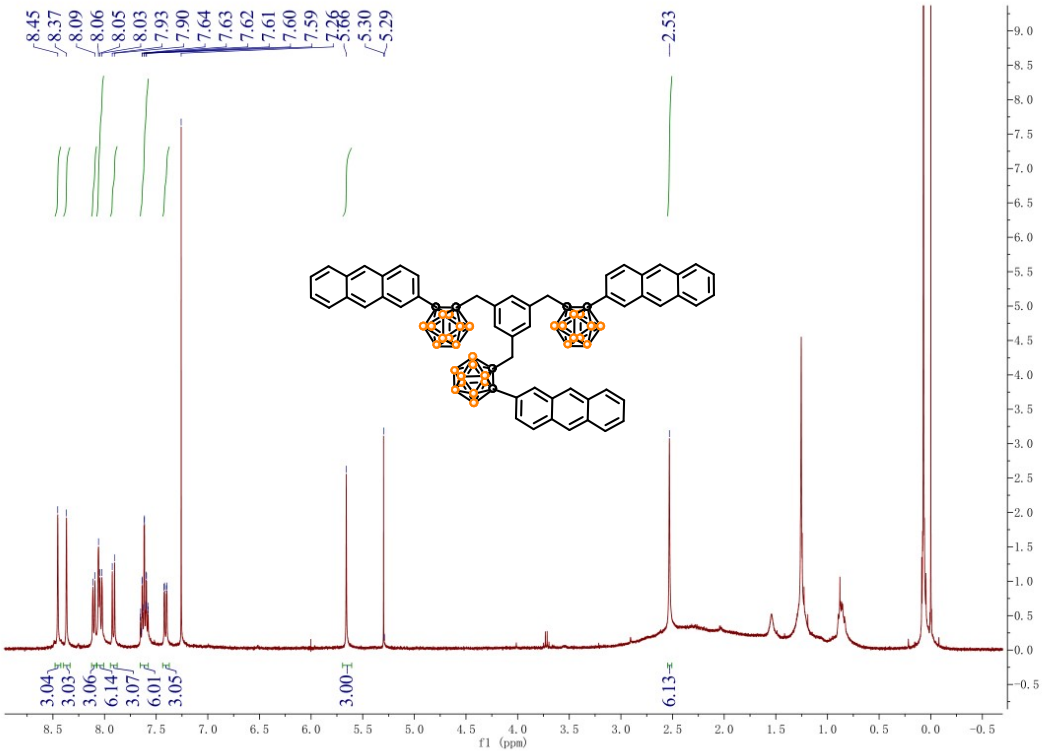

Figure S9. ^{1}H NMR spectroscopies of **CA3** in $CDCl_3$

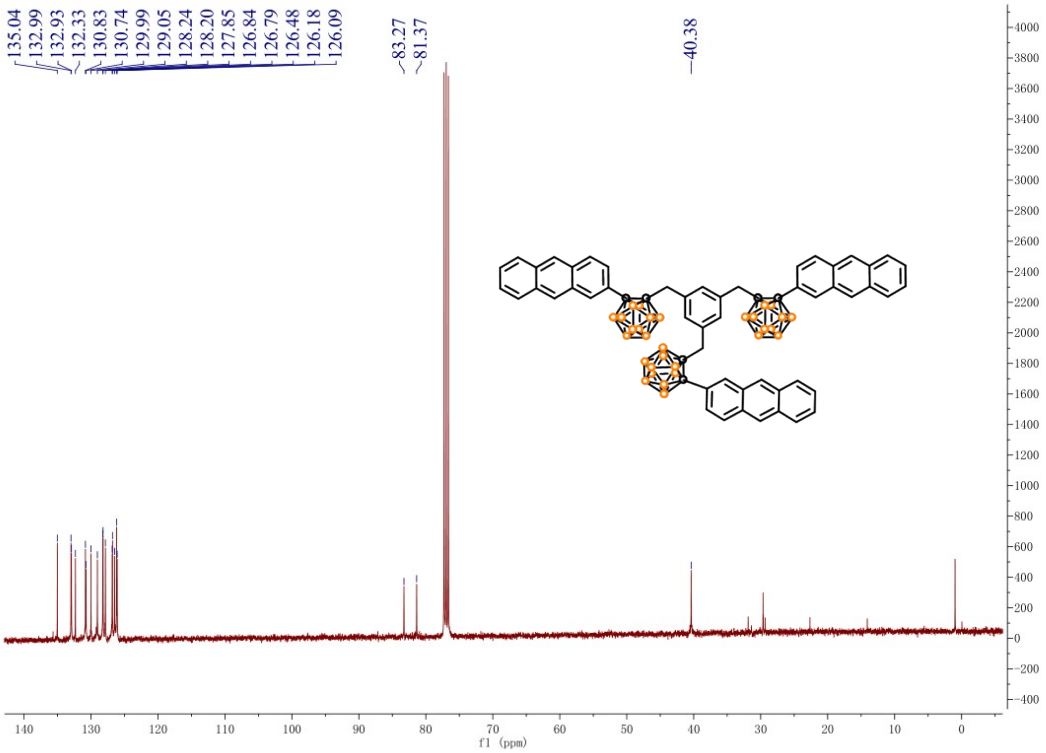

Figure S10. ^{13}C NMR spectroscopies of **CA3** in $CDCl_3$.

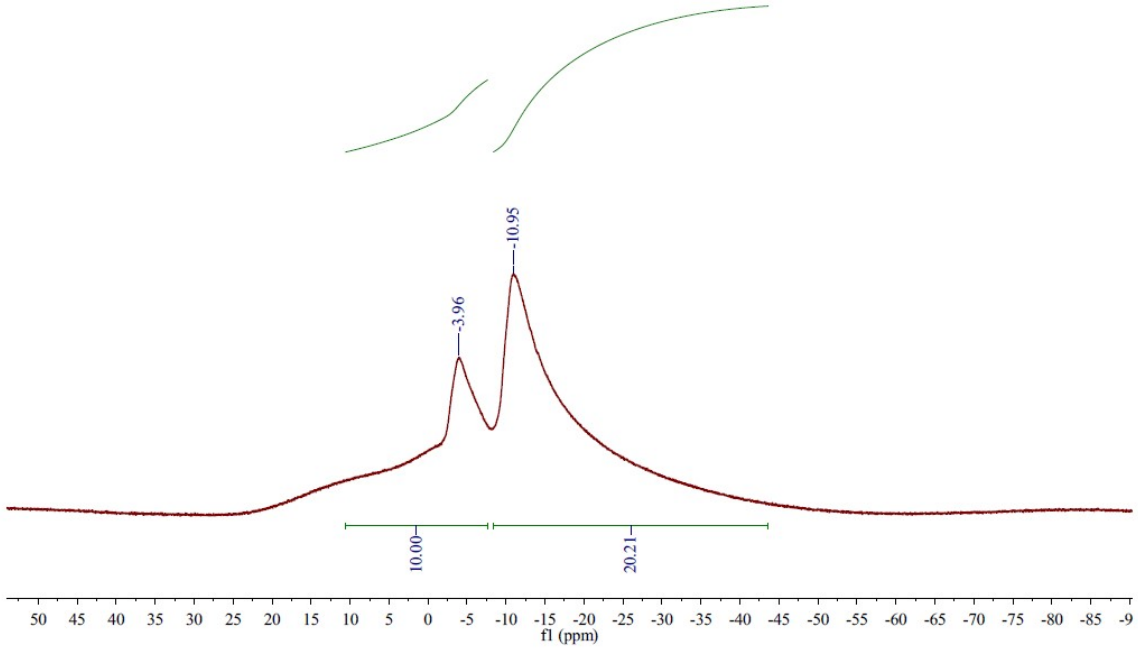

Figure S11. ^{11}B NMR spectroscopies of **CA3** in $CDCl_3$.

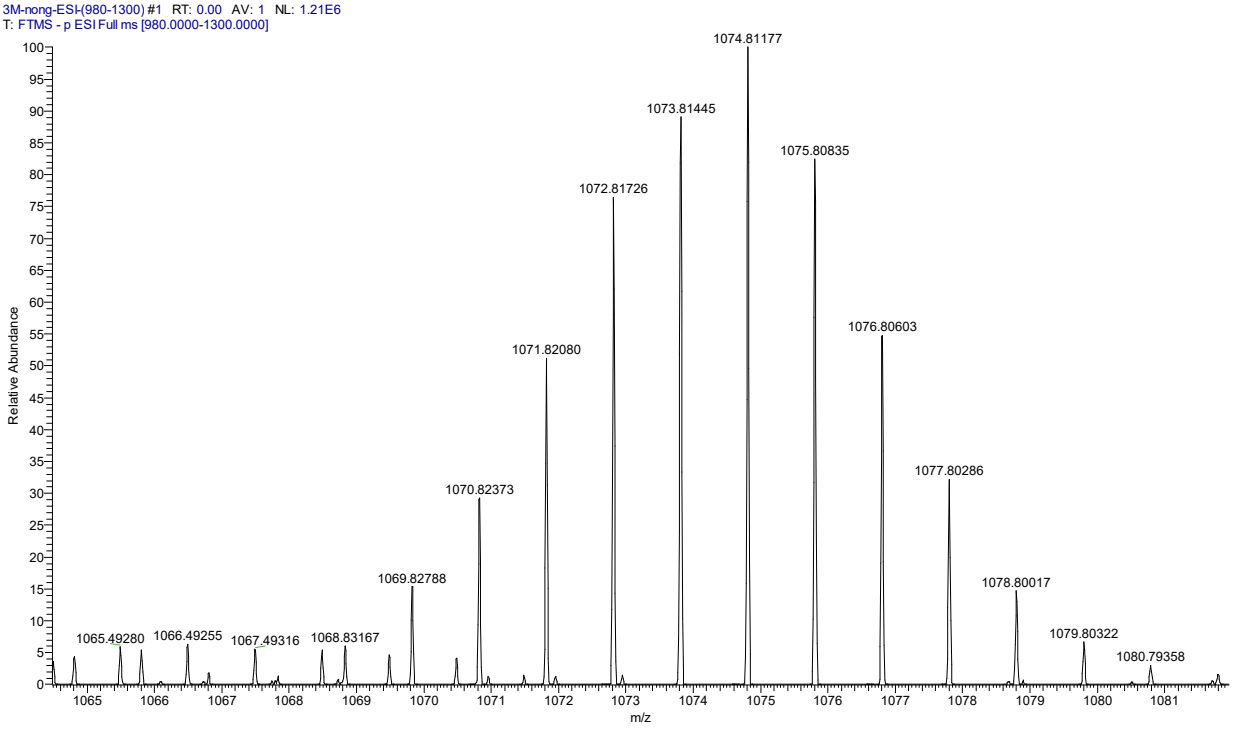

Figure S12. HRMS (ESI^-) spectrum of **CA3**

Synthesis of compound CAH

To a THF solution (5 mL) of *o*-carborane (288 mg, 2.0 mmol) was slowly added *i*−PrMgCl (1.2 M in THF, 1.2 mL, 2.4 mmol) at 0 °C under an N_2 atmosphere for 3 h, and the mixture was stirred at room temperature for 10 h. After the replacement of THF with toluene (10 mL), and addition of 2−bromanthracene (617 mg, 2.4 mmol, 1.2 eq.) and $NiCl_2$ (26 mg, 0.2 mmol) the reaction mixture was heated to 105 °C with stirring for 12 h in a closed flask. Then, the reaction was quenched with water (10 mL) and the organic layer was extracted with CH_2Cl_2 (3 × 30 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified using silica gel column chromatography using DCM/petroleum ether (1/6, v/v) as the eluent to obtain colorless compound **CAH**.

CAH：Orange yellow solid, Yield: 84%. M.p.:147.3-148.4 °C, ^{1}H NMR (400 MHz, CD_2Cl_2): ***δ*** (ppm) 8.47 (d, *J* = 8.0 Hz, 2 H), 8.19 (d, *J* = 4.0 Hz, 1 H), 8.06-8.00 (m, 3 H), 7.55–7.51 (m, 3 H), 4.25 (s, 1 H, carborane C–H), 3.18–1.60 (10 H, br, B-H). ^{13}C NMR (100 MHz, CD_2Cl_2): ***δ*** (ppm) 132.31, 133.02, 130.40, 129.82, 129.49, 128.77, 127.83, 127.77, 126.98, 126.05, 125.83, 125.75, 123.28, 76.73, 60.42. HRMS: *m/z* calcd for **[**$C_{16}H_{20}B_{10}$–H**]**$^-$: *m/z* = 321.2417. Found: *m/z* = 321.2424.

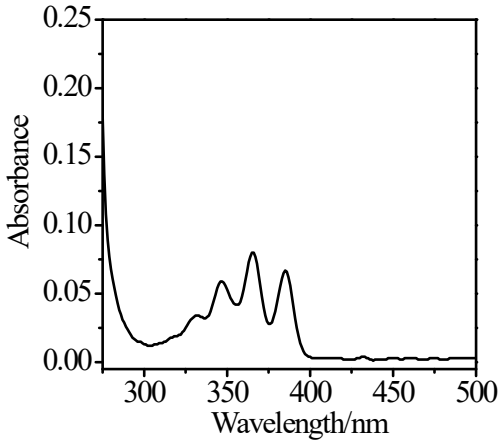

Figure S13. UV-Vis absorption spectra of **CAH** in THF solution, c=1.0×10^{-5} M, 20 °C.

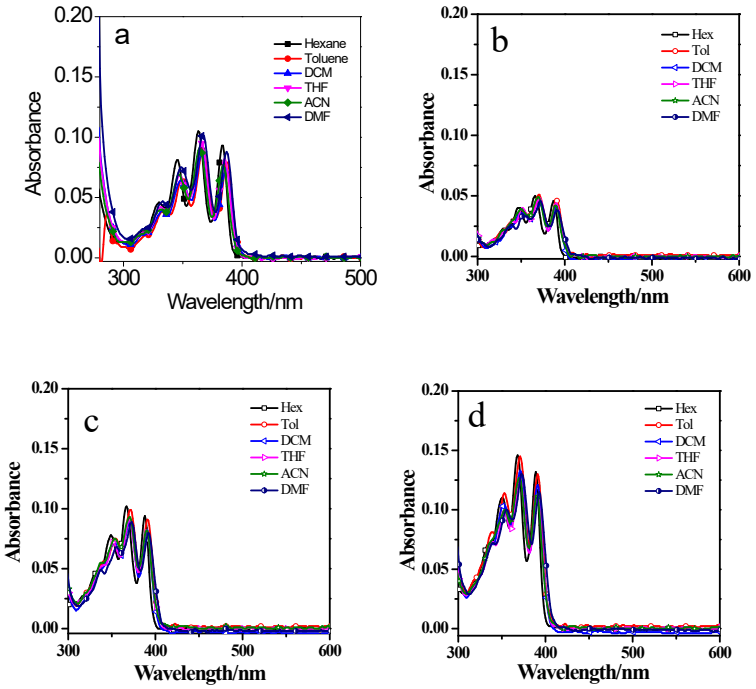

Figure S14. UV-Vis absorption of (a) **CAH**, (b) **CA1** (c) **CA3** and (d) **CA3** in different solvents. c = 1.0×10^{-5} M, 20 °C.

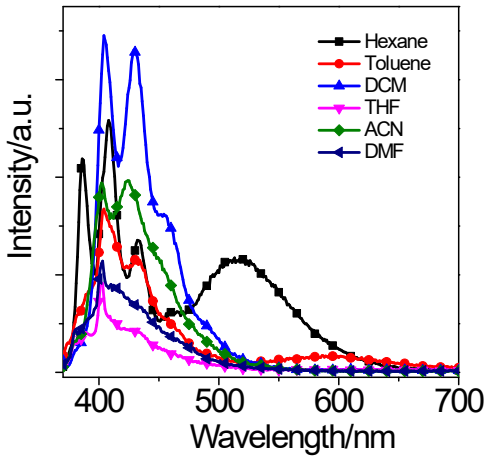

Figure S15. The emission spectra of **CAH** in various solvents, the excitation wavelength are 360 nm, c=1.0 × 10^{-5} M, 20 °C.

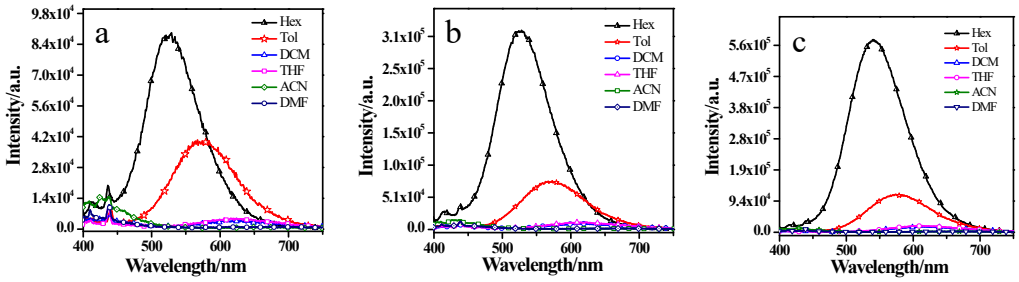

Figure S16. Fluorescence spectra of (a) **CA1**, (b) **CA2** and (c) **CA3** in different solvents. (λ_{ex}=390 nm), c = 1.0×10^{-5} M, 20 °C.

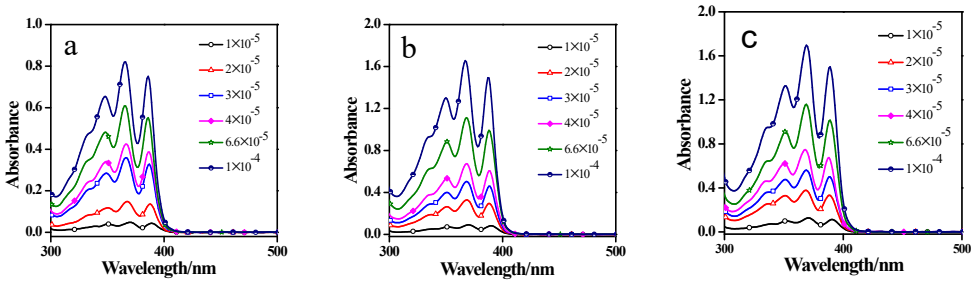

Figure S17. UV-Vis spectra of (a) **CA1**, (b) **CA2** and (c) **CA3** as a function of concentration, 20 °C.

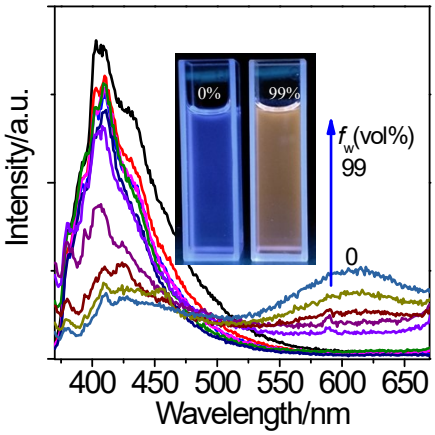

Figure S18. Fluorescence spectra of **CAH**, in THF/water mixtures with different water volume fractions (f_w), the excitation wavelength are 360 nm, c = 1.0 × 10^{-5} M, 20 °C.

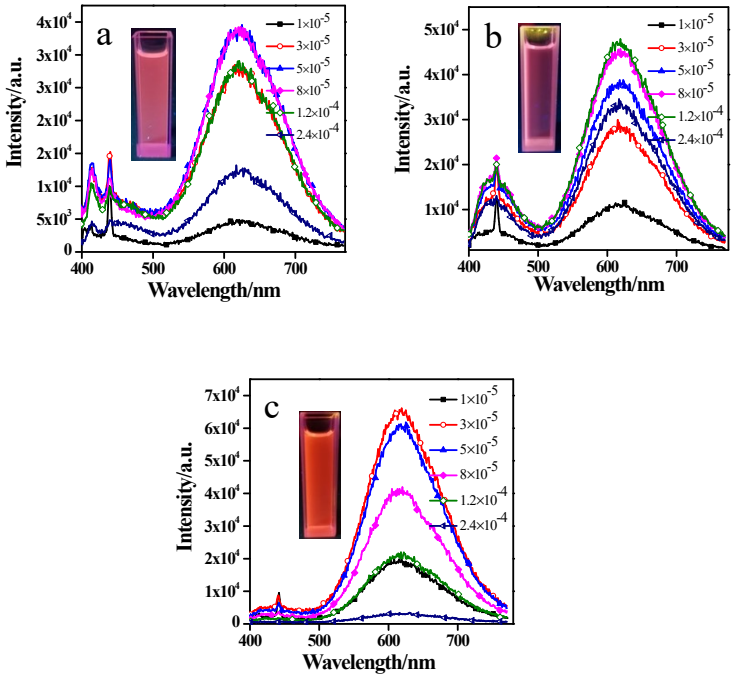

Figure S19. Fluorescence spectra of (a) **CA1**, (b) **CA2** and (c) **CA3** as a function of concentration in THF, the excitation wavelength are 390 nm, 20 °C.

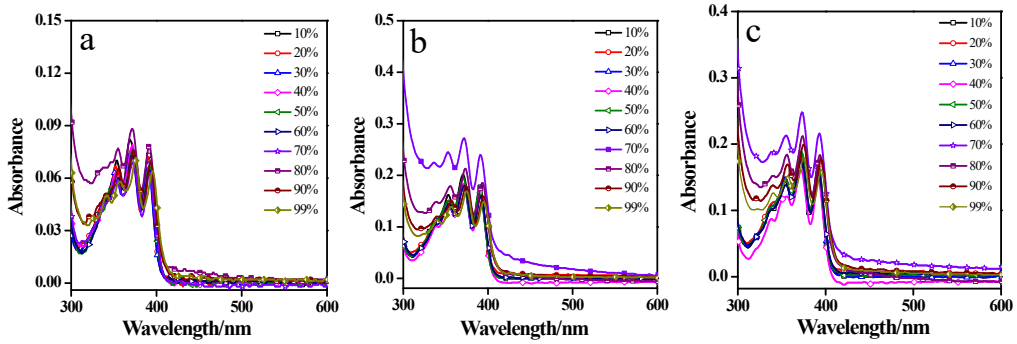

Figure S20. UV-Vis absorption of (a) **CA1**, (b) **CA2** and (c) **CA3** in solution with different water content. c = 1.0×10^{-5} M, 20 °C.

Table S1. The photophysical properties of **CAH.**

Sample	λ_{abs}(nm) [a]	λ_{em}(nm) [a,b]	τ_F(ns)[c]	Φ_F (%)	k_{rad} (10^7 s^{-1})[f]	k_{nr} (10^7 s^{-1})[f]
CAH	348, 366, 385	402, 434	3.0,[d] 2.4[e]	0.5,[a] 1.2,[d] 4.3[e]	0.4,[d] 1.8[e]	32.9,[d] 39.9[e]

[a] Measured in THF solution (1 × 10^{-5} M) at room temperature. [b] Taken by excitation at 365 nm. [c] For lifetimes excited at 370 nm. [d] f_w = 99% [e] In the solid state. [f] Values of k_{rad} and k_{nr} were calculated according to the equations, $k_{rad} = \Phi_F/\tau_F$ and $k_{nr} = (1/\tau_F)–k_{rad}$, respectively.

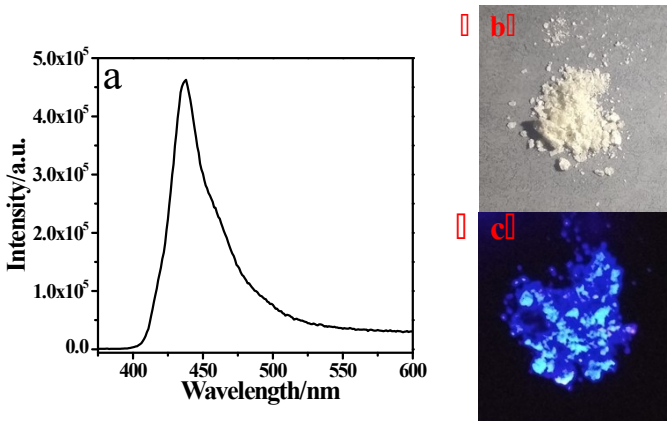

Figure S21. (a) The emission spectra of **CAH** in the solid state, λ_{ex} = 360 nm, (b) Photos of compounds **CAH** as solid powders under room light and (c) fluorescence images under UV illumination (365 nm), 20 °C.

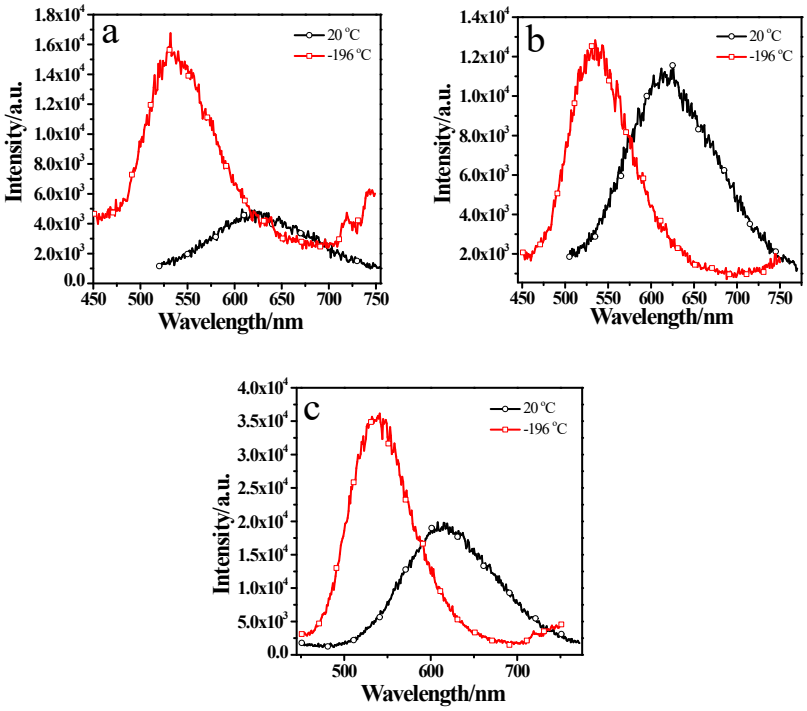

Figure S22. PL spectra of (a) **CA1**, (b) **CA2** and (c) **CA3** in 2-MeTHF at r.t. (black line) and –196 °C (red line), $c = 1.0 \times 10^{-5}$ M.

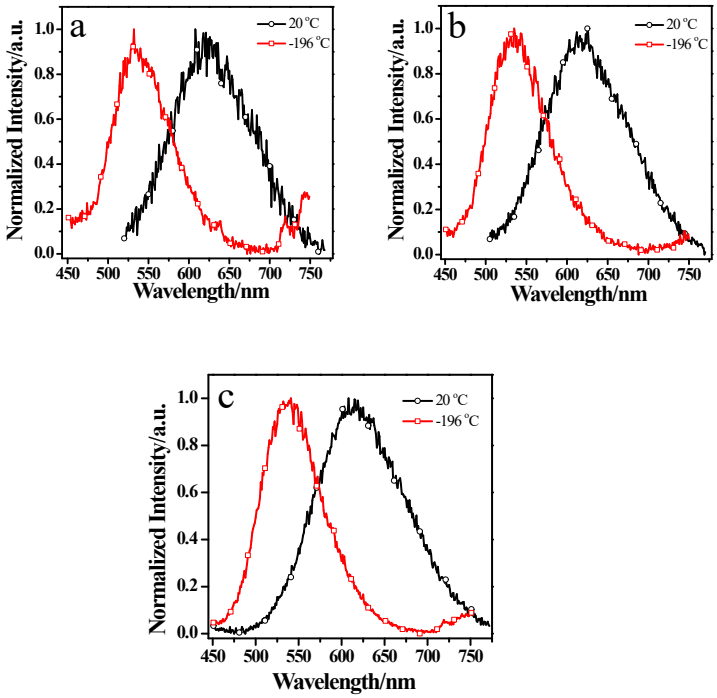

Figure S23. Normalized PL spectra of (a) **CA1**, (b) **CA2** and (c) **CA3** in 2-MeTHF at r.t. (black line) and −196 °C (red line), c = 1.0 × 10^{-5} M.

Table S2. Photoluminescence lifetime of **CA1**, **CA2** and **CA3** in different conditions.

compound	τ_f[a](ns)		
	Sol[b]	*Agg*[c]	*Solid*[d]
CA1	0.47(72.70%)	5.41(26.62%)	13.29(92.50%)
	6.68(27.30%)	14.09(73.38%	19.29(7.50%)
CA2	3.65(14.80%)	8.72(23.36%)	8.41(39.33%)
	0.81(85.20%)	20.15(76.64%)	16.94(60.67%)
CA3	0.89(43.77%)	7.78(16.92%)	8.27(36.86%)
	2.09(56.23%)	20.11(83.08%)	16.81(63.14%)

[a] Fluorescence lifetimes， [b] In THF， [c] f_w=99%, [d] In the solid state.

Table S3. Photophysical optical properties of **CA1**, **CA2** and **CA3** in various states.

Compound	*State*	K_r (10^7 s^{-1})[d]	K_{nr} (10^8 s^{-1})[d]
CA1	*Sol* [a]	0.3	4.5
	Agg [b]	2.3	0.6
	Solid [c]	2.5	0.5
CA2	*Sol* [a]	1.8	8.2
	Agg [b]	2.8	0.5
	Solid [c]	2.9	0.3
CA3	*Sol* [a]	2.0	6.1
	Agg [b]	2.4	0.5
	Sol [a]	3.8	0.2

[a] In THF， [b] f_w= 99%, [c] In the solid state， [d] Fluorescence emission rate constant (k_r) and non-radiative decay rate constant (k_{nr}) were calculated as follows: $k_r=\Phi_f/\tau_f$, $k_{nr}=(1-\Phi_f)/\tau_f$.

Table S4. Selected parameters for the UV-vis absorption and Singlet state (Fluorescence) energy of the **CA1**, **CA2** and **CA3**. Electronic excitation energies (eV), oscillator strengths (*f*), and configurations of the low-lying excited states were calculated using TDDFT//B3LYP/6-31G (d, p), based on the optimized ground state geometries.

Comp	Electronic transition [a]		TDDFT/B3LYP/6-31G (d,p)			
			Excitation energy	*f* [b]	Composition [c]	CI [d]
CA1	Abs	$S_0 \rightarrow S_1$	3.1649 eV (392 nm)	0.2454	H→L	0.6671
	Fl	$S_1 \rightarrow S_0$	2.250 eV (551 nm)	0.5641	H→L	0.7012
CA2	Abs	$S_0 \rightarrow S_1$	3.1750 eV (390 nm)	0.2354	H→L	0.6846
	Fl	$S_1 \rightarrow S_0$	2.1634 eV (573 nm)	0.2447	H→L	0.6923
CA3	Abs	$S_0 \rightarrow S_1$	3.1244 eV (397 nm)	0.3446	H→L	0.7064
	Fl	$S_1 \rightarrow S_0$	2.1903 eV (566 nm)	0.4265	H→L	0.6850

[a] Only selected excited states were considered. Numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength. [c] H stands for the HOMO and L stands for the LUMO. Only the main configurations are presented. [d] Coefficient of the wave function for each excitation. CI coefficients are given in absolute values.

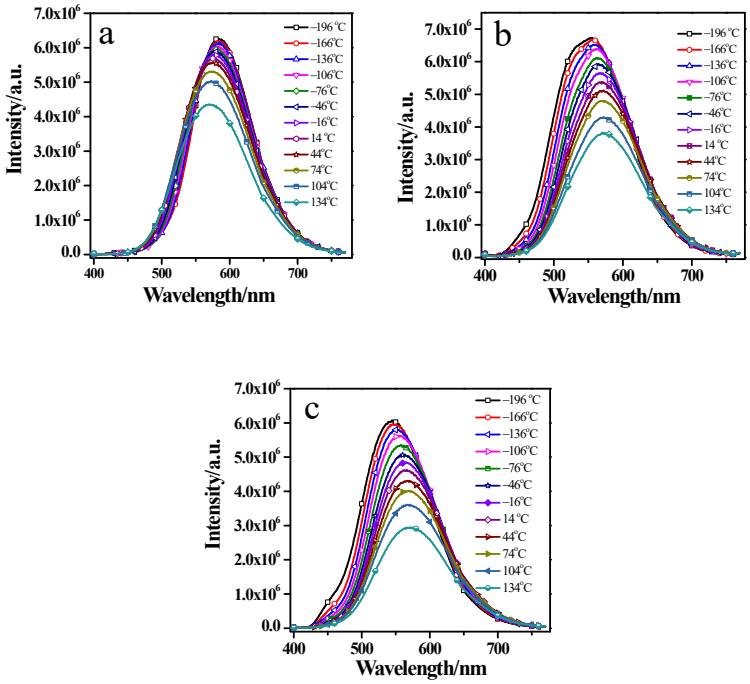

Figure S24. PL spectra of (a) **CA1**, (b) **CA2** and (c) **CA3** in the solid state during heating from −196 to 134 °C.