

# Supporting Information

## Mechanically Triggered Reversible Stepwise Tricolor Switching and Thermochromism of Anthracene-*o*-Carborane Dyad

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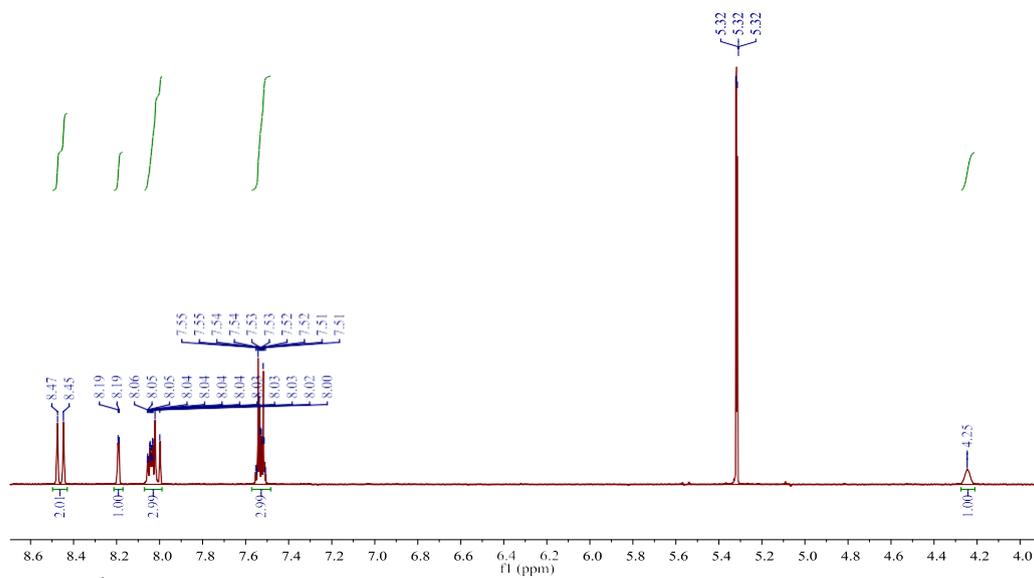


Figure S1.  $^1\text{H}$  NMR spectroscopies of pristine CAN in  $\text{CD}_2\text{Cl}_2$ .

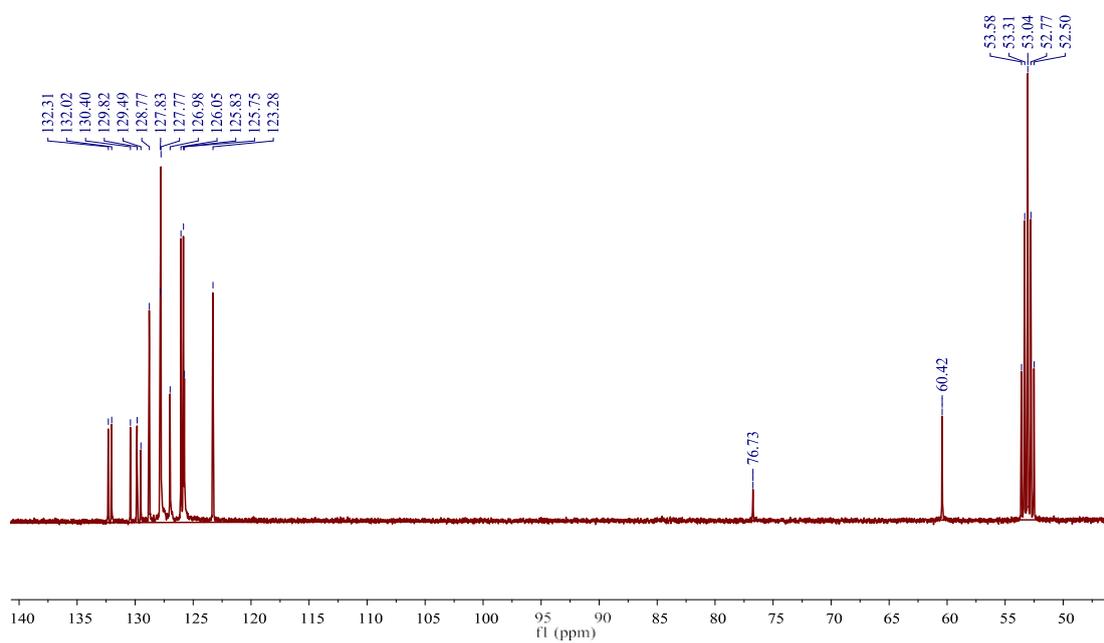
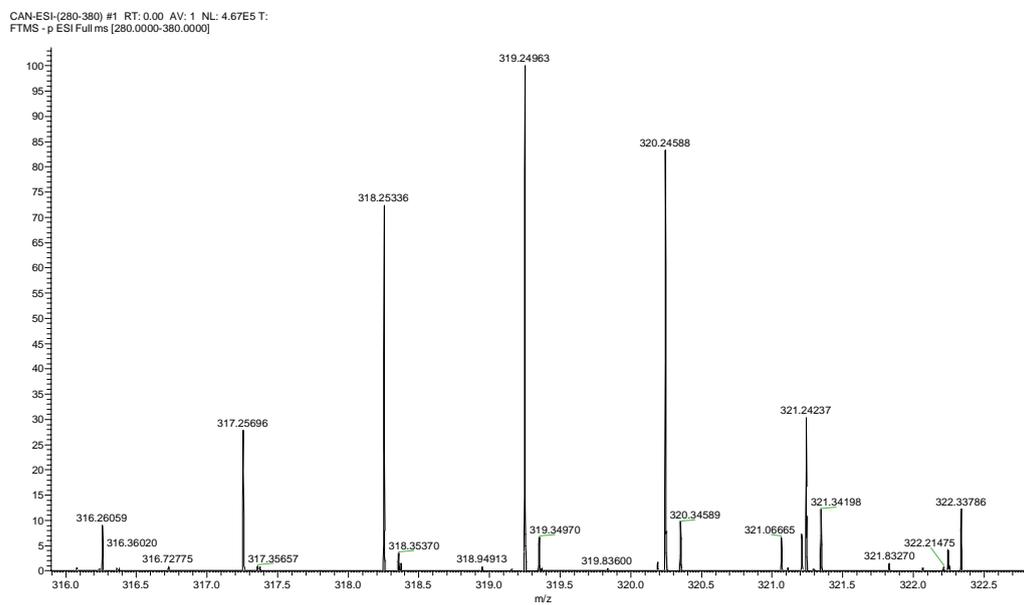
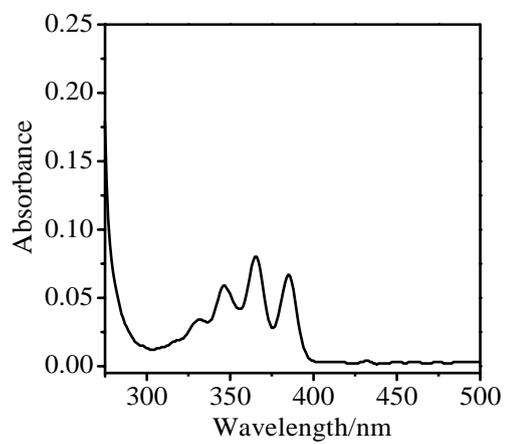


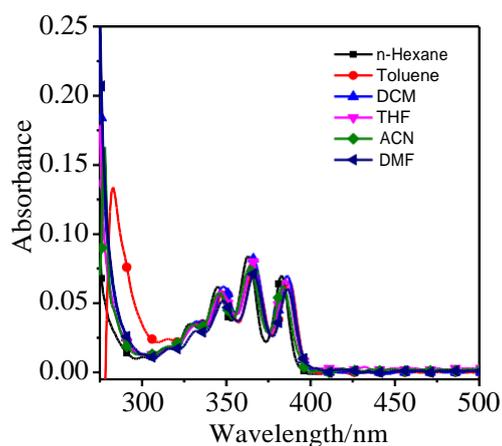
Figure S2.  $^{13}\text{C}$  NMR spectroscopies of CAN in  $\text{CD}_2\text{Cl}_2$ .



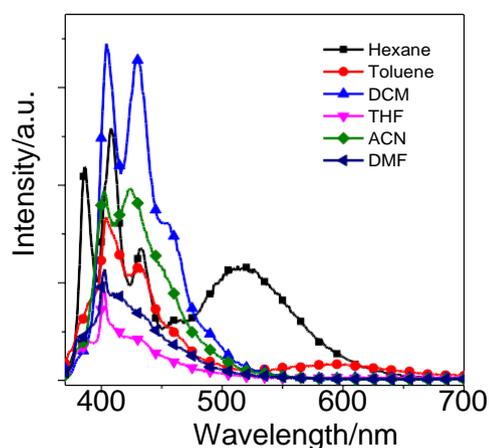
**Figure S3.** HRMS (ESI) spectrum of CAN.



**Figure S4.** UV-Vis absorption spectra of CAN in THF solution,  $c=1.0 \times 10^{-5}$  M, 20 °C.



**Figure S5.** UV-Vis absorption spectra of CAN in various solvents,  $c=1.0 \times 10^{-5}$  M, 20 °C.

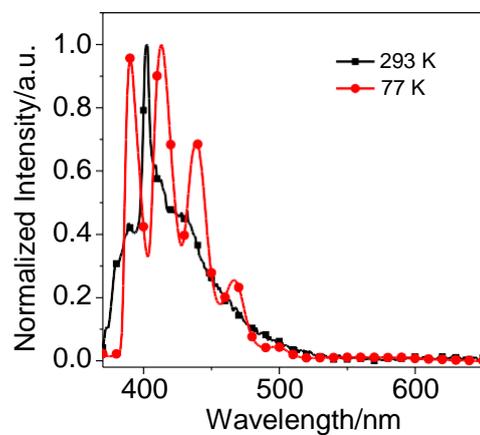


**Figure S6.** The emission spectra of CAN in various solvents, the excitation wavelength are 360 nm,  $c=1.0 \times 10^{-5}$  M, 20 °C.

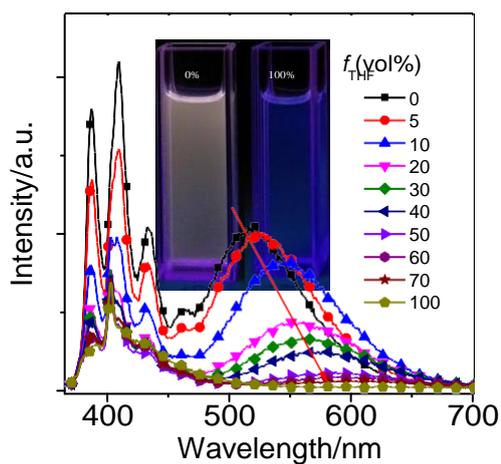
**Table S1.** The photophysical properties of CAN in different states.

Sample	State	$\lambda_{em}(nm)$ <sup>a</sup>	$\tau_F(ns)$ <sup>c</sup>	$\Phi_F$	
CAN	Solution	388, <sup>b</sup> 408, <sup>b</sup> 434, <sup>b</sup> 519 <sup>b</sup>	3.04 (0.41), 4.67 (0.59) <sup>e</sup>	0.53% <sup>d</sup> 1.2% <sup>e</sup>	
	Solid	Pristine	440	3.15 (0.59), 1.40 (0.43)	8.8%
		Slight grinding	530	5.48 (0.22), 49.9 (0.78)	14.4%
		Heavy grinding	625	6.09 (0.64), 38.8 (0.36)	4.3%

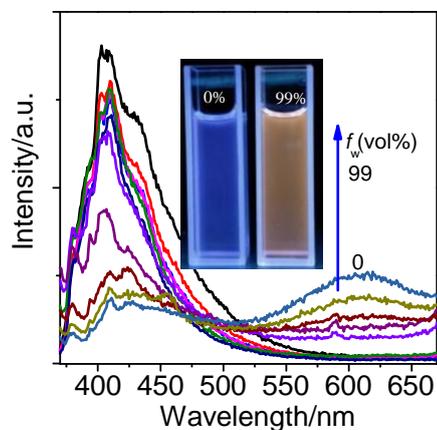
<sup>a</sup> Taken by excitation at 360 nm. <sup>b</sup> Measured in n-hexane solution ( $1 \times 10^{-3}$  M) at room temperature. <sup>c</sup> For lifetimes excited at 370 nm. <sup>d</sup> Measured in THF solution ( $1 \times 10^{-3}$  M) at room temperature. <sup>e</sup>  $f_w = 99\%$ .



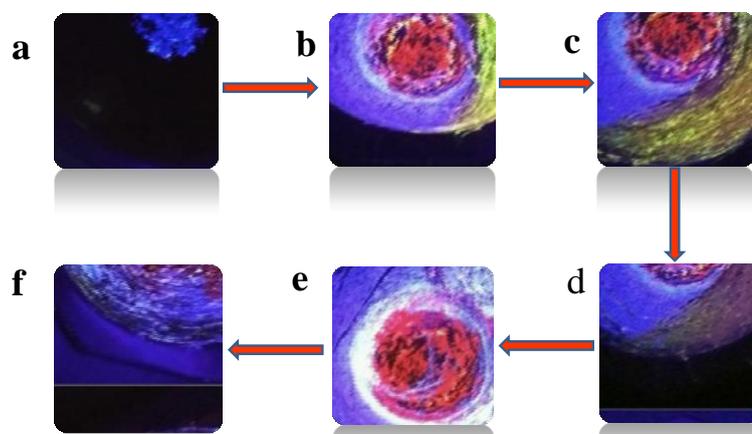
**Figure S7.** Normalized PL spectra of **CAN** in 2-MeTHF at r.t. (black line) and 77 K (red line).



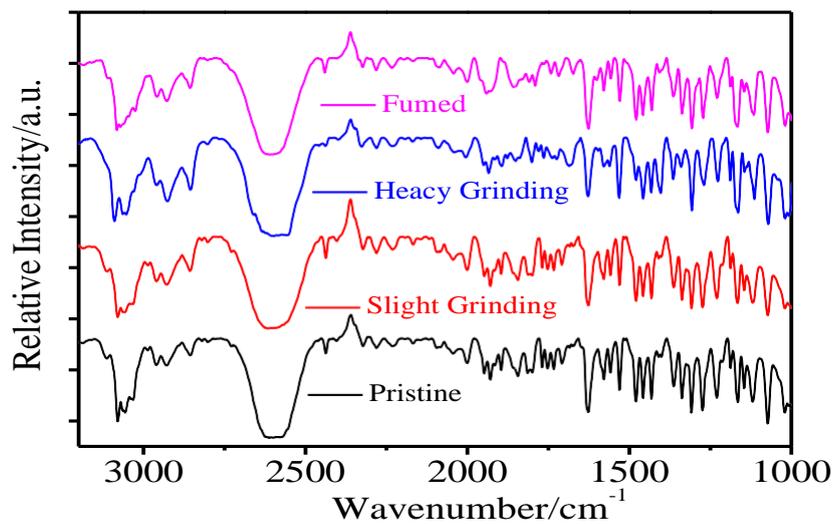
**Figure S8.** Fluorescence spectra of **CAN** in THF/n-hexane mixtures with different THF volume fractions ( $f_{\text{THF}}$ ), (The arrow indicate the change direction of emission wavelength according to the increase of THF fraction). The excitation wavelength are 360 nm,  $c=1.0 \times 10^{-5}$  M, 20 °C.



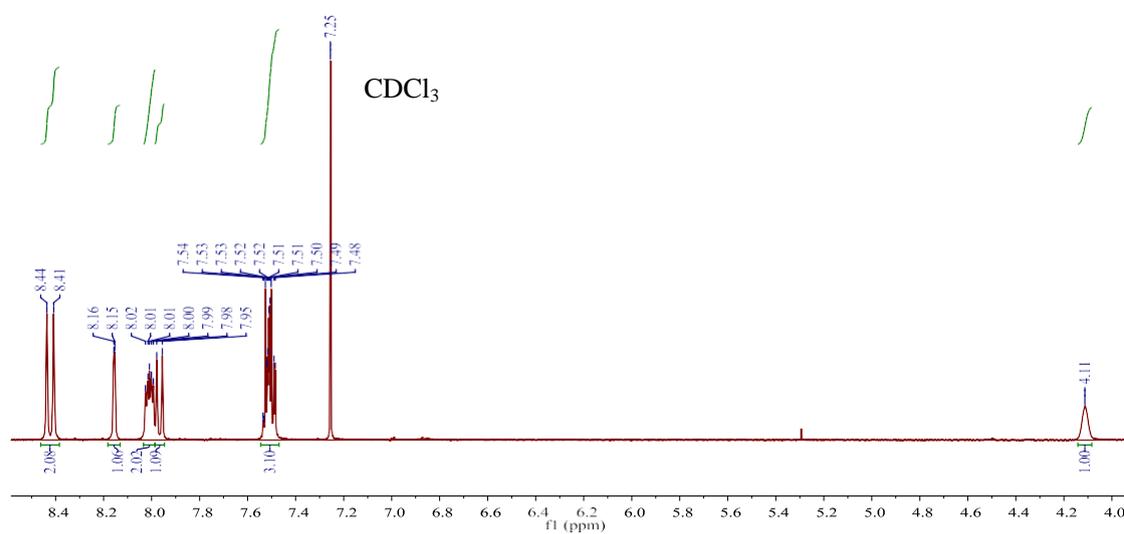
**Figure S9.** Fluorescence spectra of **CAN**, in THF/water mixtures with different water volume fractions ( $f_w$ ), the excitation wavelength are 360 nm,  $c=1.0 \times 10^{-5}$  M, 20 °C.



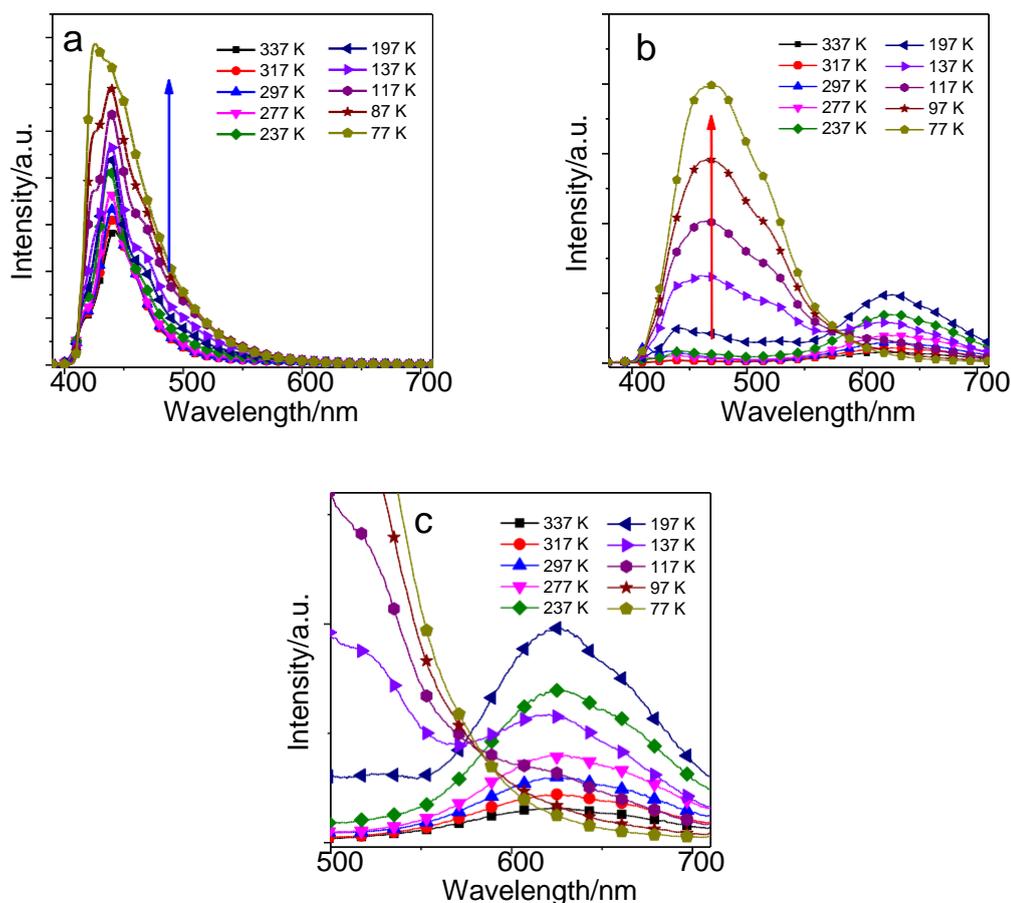
**Figure S10.** Photographs showing the emission color change of **CAN** powder with grinding or the addition of n-hexane solvent. (a) Photograph of **CAN** powder before grinding, (b) the pristine powder (left); after heavy grinding (center); after slight grinding (right); the tricolor emission emerged (c) After continues grinding, the bright yellow emission turn to reddish.(d) After heavy grinding, the bright yellow emission vanished, instead of this, the pink color emission appeared. (e) The treatment of the grinding samples with n-hexane, the pink color emission turn to blue. (f) After heavy grinding the fumed blue emission powder by n-hexane turn to the pink.



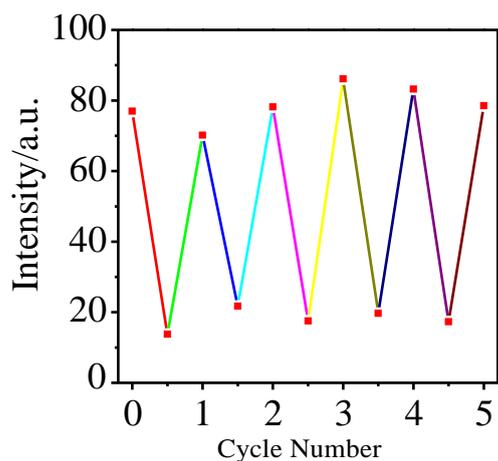
**Figure S11.** Diffuse Reflectance Fourier-Transform Infrared spectroscopy (DRIFTS) spectra of CAN powders: pristine, grinding and fumed sample (fumed with n-hexane).



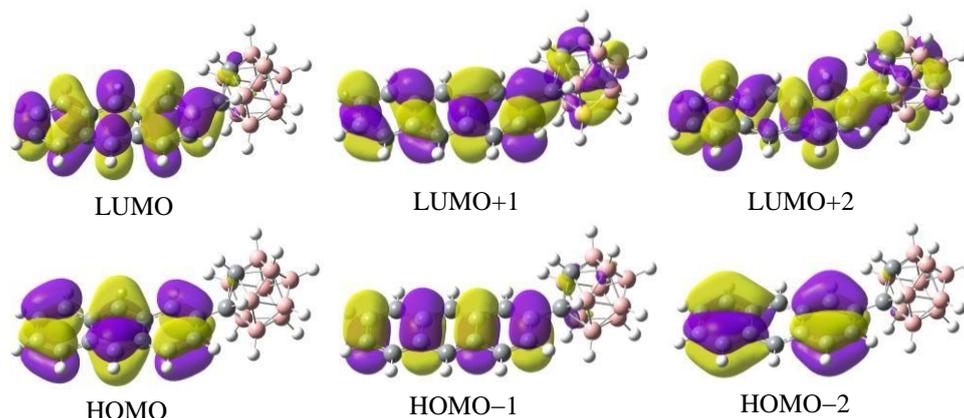
**Figure S12.** <sup>1</sup>H NMR spectroscopies of pristine CAN in CDCl<sub>3</sub>



**Figure S13.** The change of PL spectra of CAN (a) the pristine powder and (b) the heavily grinded powder heating from 77 to 333 K, (c) the drawing of partial enlargement in the PL spectra of the heavily grinded CAN powder heating from 77 to 333 K.



**Figure S14.** Reversible switching of the emission color of CAN monitored in 625 nm. (The CAN first grinding then fumed with n-hexane.)



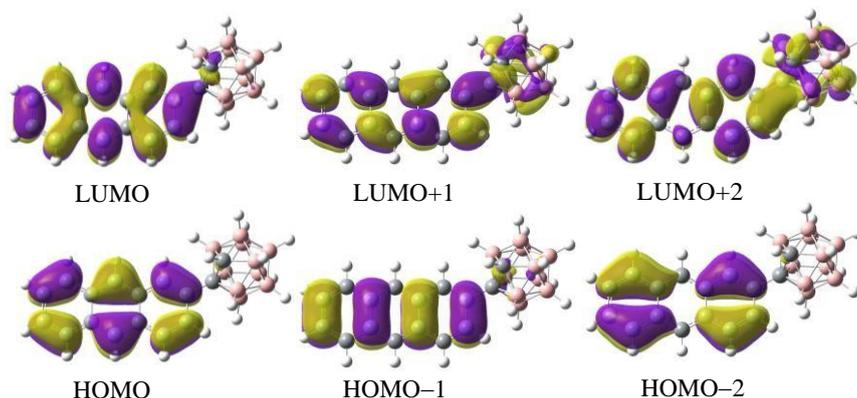
**Figure S15.** The theoretical calculated ground-state frontier orbitals contributions of **CAN** in gas phase using B3LYP/6-31G (d, p) level by Gaussian 09.

**Table S2.** Selected parameters for the UV-vis absorption and Singlet state (Fluorescence) energy of the compounds. Electronic excitation energies (eV), oscillator strengths ( $f$ ), and configurations of the low-lying excited states of **CAN** was calculated using TDDFT//B3LYP/6-31G (d, p), based on the optimized ground state geometries.

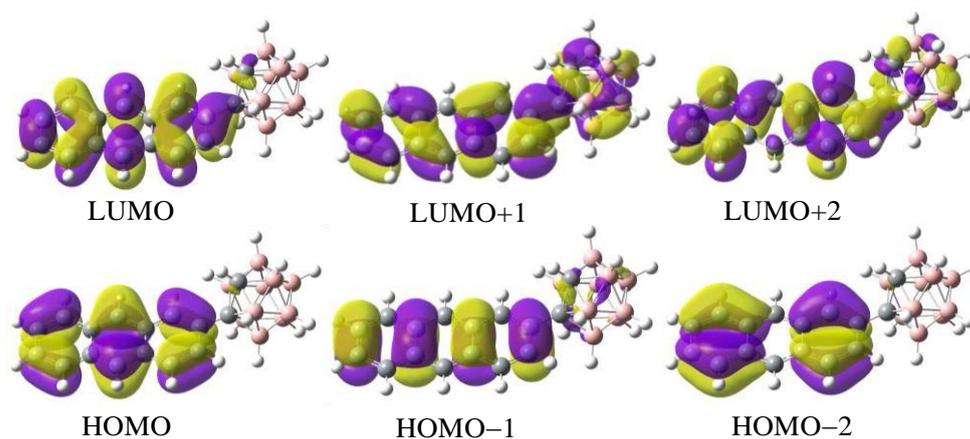
			Excitation energy <sup>a</sup>	$f$ <sup>b</sup>	Composition <sup>c</sup>	CI <sup>d</sup>
<b>CAN</b>	UV-Vis	$S_0 \rightarrow S_1$	3.1791 eV (390 nm)	0.0488	H→L	0.6991
		$S_0 \rightarrow S_2$	3.8060 eV (326 nm)	0.2135	H-1→L	0.5003
	Fluorescence	$S_0 \rightarrow S_1$	2.7763 eV (447 nm)	0.0469	H→L	0.7037

<sup>a</sup> Only selected excited states were considered. Numbers in parentheses are the excitation energy in wavelength. <sup>b</sup>

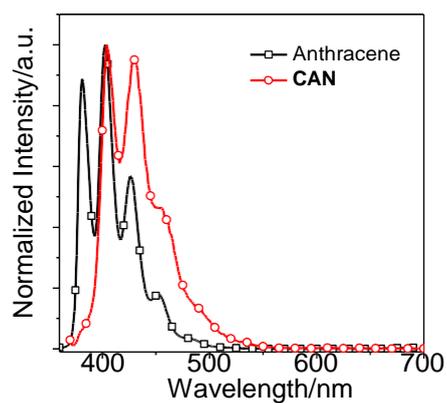
Oscillator strength. <sup>c</sup> H stands for the HOMO and L stands for the LUMO. Only the main configurations are presented. <sup>d</sup> Coefficient of the wave function for each excitation. CI coefficients are given in absolute values.



**Figure S16.** The theoretical calculated UV-vis absorption frontier orbitals contributions of **CAN** in gas phase estimated by TD-DFT calculation at the B3LYP/6-31G (d, p) level by Gaussian 09.



**Figure S17.** The theoretical calculated singlet state (Fluorescence) frontier orbitals contributions of CAN in gas state estimated by TD-DFT calculation at the B3LYP/6-31G (d, p) level by Gaussian 09.



**Figure S18.** The emission spectra of CAN and anthracene in DCM, the excitation wavelength are 360 nm,  $c = 1.0 \times 10^{-5}$  M, 20 °C.

The photoluminescence (PL) spectra were recorded in DCM (Figure S18). CAN showed vibrational bands at  $\lambda = 389$  and 430 nm, and these bands are analogous to that of anthracene monomer in solution. Therefore, the emission from CAN in DCM solution could be assigned to emission from the LE state of the anthracene moiety.