

利用邻-碳硼烷可变的 C-C 键实现发光分子从 ACQ 到 AIE 转变

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摘要: 利用邻-碳硼烷骨架中可变的 C-C 键, 将在聚集态会发生猝灭(ACQ)的传统发光分子和具有振动自由度的碳硼烷基团连接起来, 合成了带有聚集诱导发光(AIE)效应的邻-碳硼烷基发光分子。通过紫外可见吸收光谱、DFT 计算、发射光谱及晶体结构测定等手段, 研究了邻-碳硼烷可变的 C-C 键对化合物性质的影响。结果表明, 在邻-碳硼烷骨架的碳原子上引入不同的取代基可以改变 C-C 键的振动特性, 从而能够调控化合物的发光性质, 并有效实现从 ACQ 到 AIE 的转变。

关键词: 碳硼烷; 聚集诱导猝灭; 聚集诱导发光

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Transform ACQ Luminophores to AIEgens via Engineering the Variable C-C Bonds of *o*-Carboranes in Fluorescent Cores

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Abstract: The variable C-C bond of *o*-carborane cage was treated as a vibrational factor. A temptation to synthesize AIE-active *o*-carborane luminophores were carried out via coupling *o*-carborane with conventional luminophores who suffered from ACQ (aggregation-caused quenching) effect. Meanwhile, the photophysical properties were investigated by UV-Vis spectra, DFT calculations, PL spectra and crystal structure analysis. The results indicate that different substituents (H, ethyl and phenyl) in *o*-carboranes could remarkably affect its vibration performance. Ultimately, photophysical properties can be tuned from ACQ to AIE. CCDC: 1834185, ***o*-me-an**; 1834186, ***ph-o-an***; 1838538, ***o-et-an***.

Keywords: carborane; aggregation-caused quenching; aggregation-induced emission

0 Introduction

Usually, bright luminescence from luminophores in solutions is absent^[1-3] upon aggregation. Such aggregation-caused quenching (ACQ) effect is triggered by

intermolecular interactions^[4] such as $\pi \cdots \pi$ stacking or excimers, further causing a detrimental effect on luminous efficiency^[5-7], thus badly fulfill the needs of various applications. In stark contrast to ACQ, another unique photophysical phenomenon termed as

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aggregation-induced emission (AIE) established by Tang^[8] shows excellent photophysical properties. In the past 20 years, AIE has become a significant principle to construct luminophores^[9-11] in material science and biological technology. Generally, luminophores possessing AIE properties can be accessed via the restriction of intramolecular motion (RIM)^[12], which blocks the non-radiative pathway and produces effective luminescence in aggregates. Therefore, direct transformation of conventional ACQ luminophores to AIE luminogens (AIEgens) will be a best choice to obtain AIEgens by embedding sufficient intramolecular motions^[13]. From this point of view, AIEgens can be generated by modifying luminophores with well-known AIE archetypes^[14-15] or in the other way replacing parts of AIE molecules with classical luminophores^[16-17]. Despite these pioneering tactics and enormous AIE-active compounds in hand, some systems^[18] remain to suffer from complicated molecular design and tedious synthetic procedures to cater for the requirements of various high-tech applications. Therefore, it is to be the theme to develop a novel strategy to realize efficient AIEgens.

Recently, luminophores containing *o*-carborane unit for photoelectric functional materials^[19-20] have drawn much attention. The unique properties of *o*-carborane^[21], such as polarizable σ -aromatic character and electron-withdrawing ability through substitution at the carbon sites, make excellent properties with satisfactory stability and fantastic luminous efficiency. For example, Kang et al.^[22] revealed that CT (charge transfer) emissions in *o*-carborane-based luminophores originate from the orbital overlap between the chromophores and the carboranyl σ (C-C) orbitals. Chujo et al.^[23] reported that the AIE properties of a variety of *o*-carborane-based conjugated systems were caused by intramolecular charge transfer from the π -conjugated groups to *o*-carborane. Lee et al.^[24] indicated by experiments that the phosphorescence efficiency of iridium complexes could be manipulated by the substituents at carbon sites in *o*-carborane, and the carboranyl C-C bond vibration in the excited state would be responsible for phosphorescence efficiency. Our group^[25] has

previously demonstrated the luminescent efficiency of *o*-carborane-based iridium complexes exhibit solvent- or media-dependence, which is closely related to dielectric constant of media. It can be concluded that the variable C-C bond of *o*-carborane might be a useful tool to tune the photophysical properties of luminophores.

Besides aforementioned results, theoretical calculations^[26] also uncovered that the C-C bond lengths of *o*-carborane could vary substantially with the nature of the carbon substituents. It should be anticipated that the vibrating motion of the C-C bond in *o*-carborane can provide a radiationless channel by modifying the substituents (such as alkyl and phenyl)^[27], which result in weak luminescence in solution. However, the cage structure can suppress both the $\pi \cdots \pi$ stacking and the C-C bond vibration in aggregate state^[28-29], thus giving rise to enhanced emissions with AIE properties. Such characteristic of the C-C bond in *o*-carborane could be the new strategy to realize transformation from ACQ luminophores to AIEgens. Herein, in order to confirm this idea, phenyl anthracene undergoing ACQ properties was designed with *o*-carborane cage bearing different substituents. Photophysical properties indicated that these compounds undergo the similar emission behavior in solution. However, the luminophores only with the substituents ethyl and phenyl in *o*-carborane show AIE properties. This observation can be ascribed to the elongation of C-C bond that dissipate the energy in excited state, and to the more rigid packing structures in crystalline state^[30], leading to the transformation from ACQ luminophores to AIEgens.

1 Experimental

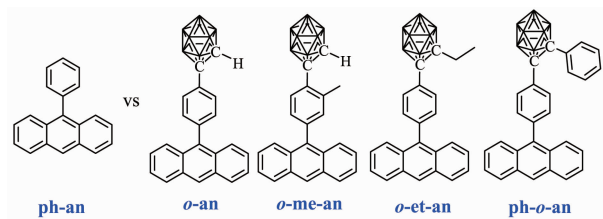
1.1 General

All starting materials were purchased from commercial sources and were used directly without further purification. Reactions were carried out under an argon atmosphere using standard Schlenk procedure. The ¹H, ¹³C, ¹¹B NMR spectra were measured on DRX-400 at room temperature with CDCl₃ as a deuterated reagent. Mass spectra were tested with a Bruker

Daltonics Autoflex II MALDI TOF MS spectrometer and a Micromass GC-TOF for EI-MS (70 eV) spectrometer. Infrared spectra were performed on a Nicolet NEXUS870 FT-IR. UV-Vis absorption spectra were recorded with Shimadzu UV-2550 spectrophotometers. PL spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer.

1.2 Synthesis

All of the *o*-carborane-functionalized compounds (Scheme 1) were synthesized using *o*-carborane substituted halide as a starting material through the Suzuki reaction^[31] (Supporting Information, Scheme S1). All the newly synthesized compounds are stable to air and light. These compounds were carefully characterized by NMR, MS and IR. Besides, the crystal structures of all the *o*-carborane-based compounds were solved via X-ray crystallography (Fig.S13).



Scheme 1 Illustration of *o*-carborane-functionalized anthracene derivatives

1-(4-bromophenyl)-2-ethyl-*o*-carborane (**1-et**): A DMF solution of 1-(4-bromophenyl)-*o*-carborane (299 mg, 1.0 mmol) was treated with sodium hydride (90.0 mg, 2.4 mmol) at $-20\text{ }^{\circ}\text{C}$. After stirring for 1 h, an excess amount of $\text{C}_2\text{H}_5\text{I}$ (1.5 equiv, 1.5 mmol) was added into the above mixture. The reaction was stirred for another 4 h. After quenching the reaction mixture by saturated ammonium chloride solution (20.0 mL), the aqueous layer was extracted with diethyl ether (three times). Combined organic layers were filtered, dried over MgSO_4 , and concentrated under reduced pressure. Further purification was performed by column chromatography on silica. Elution with *n*-hexane gave white solid with a yield of 50% (160.3 mg). ^1H NMR (400 MHz, chloroform-*d*): δ 7.55~7.46 (m, 4H), 3.25~1.70 (br, 10H, B-H), 1.88~1.82 (m, 2H), 0.98 (t, $J=7.6$ Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 132.64, 132.11, 129.99, 125.52, 83.24, 28.71, 13.85. ^{11}B NMR

(128 MHz, chloroform-*d*): δ -2.92 (1B), -4.10 (1B), -10.47 (8B). Anal. Calcd. for $\text{C}_{10}\text{H}_{19}\text{B}_{10}\text{Br}$ (%): C, 36.70; H, 5.85. Found(%): C, 37.47; H, 5.46. IR (KBr, cm^{-1}): 2 583 (B-H). EI-MS (m/z): 327.23 (M^+ , 100.00%).

o-et-an: A mixture of **1-et** (100.0 mg, 0.31 mmol) and 9-anthraceneboronic acid (81.4 mg, 0.37 mmol), $\text{Pd}(\text{P}(\text{Ph})_3)_4$ (23.1 mg, 0.02 mmol), K_2CO_3 (84.5 mg, 0.62 mmol) in THF (20.0 mL) was refluxed for 48 h under argon. After cooling down to r.t., water (40.0 mL) was added. Then, the resulting mixture was extracted with CH_2Cl_2 (3×30 mL) and the combined organic layers were dried on MgSO_4 . Removal of the solvents in vacuum gave a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane gave white solid with a yield of 36% (47.4 mg). ^1H NMR (400 MHz, chloroform-*d*): δ 8.54 (s, 1H), 8.07 (d, $J=8.4$ Hz, 2H), 7.84 (d, $J=8.4$ Hz, 2H), 7.55~7.46 (m, 4H), 7.40~7.31 (m, 4H), 3.25~1.70 (br, 10H, B-H), 2.06 (q, $J=7.5$ Hz, 2H), 1.12 (t, $J=7.6$ Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 141.55, 134.86, 131.82, 131.31, 131.19, 130.12, 129.89, 128.57, 127.35, 126.15, 125.86, 125.29, 83.44, 28.91, 14.02. ^{11}B NMR (128 MHz, chloroform-*d*): δ -3.09 (1B), -4.17 (1B), -9.69(4B), -10.60(4B). Anal. Calcd. for $\text{C}_{24}\text{H}_{28}\text{B}_{10}$ (%): C, 67.89; H, 6.65. Found (%): C, 67.55; H, 6.32. IR (KB, cm^{-1}): 2 563 (B-H). MALDI-TOF(m/z): 424.56 (M^+).

ph-o-an was synthesized by the same procedure as that of **o-et-an**. White solid, 58.6 mg, with a yield of 40%. ^1H NMR (400 MHz, chloroform-*d*): δ 8.47 (s, 1H), 8.02 (d, $J=8.5$ Hz, 2H), 7.64~7.59 (m, 2H), 7.55~7.51 (m, 2H), 7.47~7.42 (m, 2H), 7.36 (m, 1H), 7.32~7.26 (m, 4H), 7.24~7.17 (m, 4H), 3.25~1.70 (br, 10H, B-H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 141.06, 131.18, 131.06, 130.84, 130.80, 130.06, 129.74, 128.44, 128.25, 127.08, 126.12, 125.56, 125.16. ^{11}B NMR (128 MHz, chloroform-*d*): δ -2.22 (3B), -9.26 (3B), -10.31 (4B). Anal. Calcd. for $\text{C}_{28}\text{H}_{28}\text{B}_{10}$ (%): C, 71.15; H, 5.97. Found(%): 70.88; H, 5.53. IR (KBr, cm^{-1}): 2 593 (B-H). MALDI-TOF (m/z): 472.53 (M^+).

o-me-an was synthesized by the same procedure as that of **o-et-an**. White solid, 38.1 mg, with a yield of 30%. ^1H NMR (400 MHz, chloroform-*d*): δ 8.52 (s, 1H), 8.05 (d, $J=8.4$ Hz, 2H), 7.76 (d, $J=8.3$ Hz, 1H),

7.59 (d, $J=8.8$ Hz, 2H), 7.50~7.45 (m, 2H), 7.41~7.36 (m, 2H), 7.29 (dd, $J=8.3, 1.7$ Hz, 1H), 7.21 (s, 1H), 4.69 (s, 1H), 3.25~1.70 (br, 10H, B-H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 140.16, 136.44, 134.99, 134.79, 131.34, 131.27, 131.16, 129.91, 129.70, 128.49, 127.41, 127.15, 126.32, 125.73, 125.24, 78.09, 77.35, 77.03, 76.71, 59.89, 23.37. ^{11}B NMR (128 MHz, chloroform- d): δ -2.70 (2B), -8.66 (4B), -11.09 (2B), -13.11 (2B). Anal. Calcd. for $\text{C}_{23}\text{H}_{26}\text{B}_{10}$ (%): C, 67.28; H, 6.38. Found(%): 67.21; H, 6.08. IR (KBr, cm^{-1}): 2 571 (B-H). MALDI-TOF(m/z): 410.54 (M^+).

1.3 X-ray crystal structure determination

X-ray diffraction data were collected on a Bruker Smart CCD Apex DUO diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) using the ω - 2θ scan mode. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined on F^2 by full-

matrix least-squares methods using SHELXTL-2016. All calculations and molecular graphics were carried out on a computer using the SHELX-2016 program package and Diamond. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically and refined isotropically using the riding model. Crystal data, data collection parameters and the results of the analyses of ***o*-et-an**, ***ph*-*o*-an** and ***o*-me-an** are listed in Table 1.

CCDC: 1834185, ***o*-me-an**; 1834186, ***ph*-*o*-an**; 1838538, ***o*-et-an**.

2 Results and discussion

2.1 Photophysical studies

To check whether *o*-carboranyl unit can tune the emission behavior in comparison to the model compound (Scheme 1), photophysical properties of all the compounds were investigated. The absorption

Table 1 Crystallographic data for ***o*-et-an**, ***ph*-*o*-an** and ***o*-me-an**

Compound	<i>o</i>-et-an	<i>ph</i>-<i>o</i>-an	<i>o</i>-me-an
Chemical formula	$\text{C}_{23}\text{H}_{26}\text{B}_{10}$	$\text{C}_{28}\text{H}_{28}\text{B}_{10}$	$\text{C}_{23}\text{H}_{26}\text{B}_{10}$
Formula weight	424.56	472.60	410.54
Temperature / K	296(2)	293(2)	296(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a / nm	0.825 73(17)	0.987 72(19)	1.025 4(3)
b / nm	2.473 2(5)	2.955 7(5)	1.065 3(3)
c / nm	2.591 4(5)	1.861 5(3)	2.038 9(6)
α / ($^\circ$)	65.840(3)		
β / ($^\circ$)	85.881(4)	106.699(8)	90.245(4)
γ / ($^\circ$)	87.488(4)		
V / nm^3	4.815 6(17)	5.205 3(16)	2.227 2(11)
Z	8	8	4
D_c / ($\text{g}\cdot\text{cm}^{-3}$)	1.171	1.206	1.224
μ / mm^{-1}	0.060	0.062	0.062
$F(000)$	1 704	1 968.0	856.0
θ range / ($^\circ$)	0.863~24.999	1.334~24.999	1.998~25.000
Reflection collected, unique	34 433, 16 269 ($R_{\text{int}}=0.104$ 8)	39 079, 9 156 ($R_{\text{int}}=0.128$ 3)	15 966, 3 891 ($R_{\text{int}}=0.045$ 5)
Completeness to $\theta=25.000^\circ$ / %	95.9	99.9	99.3
Data, restraint, parameter	16 269, 6, 1 229	9 156, 0, 686	3 891, 0, 343
GOF	0.981	1.007	1.147
Final R indices [$I>2\sigma(I)$]	$R_1=0.113$ 1, $wR_2=0.280$ 2	$R_1=0.069$ 2, $wR_2=0.186$ 1	$R_1=0.045$ 7, $wR_2=0.139$ 0
R indices (all data)	$R_1=0.225$ 4, $wR_2=0.352$ 7	$R_1=0.119$ 5, $wR_2=0.241$ 3	$R_1=0.053$ 8, $wR_2=0.159$ 2
Largest diff. peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	650 and -380	351 and -354	288 and -265

spectra were measured in THF solution (Fig.S15). However, no apparent change is observed^[32]. All the compounds exhibit two bands due to π - π^* transitions^[33]: one is the sharp absorption band at *ca.* 260 nm, and the other shapes as three weak bands from *ca.* 340 to 400 nm. Thus, the introduction of *o*-carborane shows very little effect upon the anthracene unit in absorption measurements, which were proven by DFT (density functional theory) calculations (Fig.S24). Besides, all *o*-carborane-based compounds exhibit similar absorption spectra compared to that of the model compound in non-polar solvents, such as *n*-hexane and toluene (Fig. S16 and S17). Thus, the polarity of solvent does not change the ground state energy of these luminophores.

Photoluminescence (PL) spectra were then investigated in THF solution. Compounds ***o*-an**^[31], ***o*-me-an**, and ***o*-et-an** display the similar PL spectra as that of **ph-an**, whereas the control compound is much more emissive (Fig.1). This could be ascribed to the variable C-C bond in *o*-carboranyl unit which is involved in the excited state to dissipate energy. Such variation of luminous efficiency is in accordance with reported results^[30]. To get in-depth insights, the excited state structures for all the compounds have been investigated. During emission process, the larger C-C bond length variation in *o*-carborane was observed (Table S2). This adequately indicates that the C-C bond variation leads to a non-radiative decay from the excited states^[34-35]. In addition, PL spectra in lower polarity solvent as toluene were studied, which exhibit dual emissions (Fig.2) around 410 and 600 nm, attributed to LE (locally-excited) emission from phenyl anthracene and ICT(intramolecular charge transfer) emission from anthracene to *o*-carborane, respectively. This reveals that *o*-carborane can be the electron acceptor to induce intramolecular charge transfer^[36-37]. However, compound **ph-*o*-an** presents only CT emission. Theoretical calculations show that the highest occupied molecular orbitals (HOMOs) of these compounds locate in the anthracenyl units, whereas the lowest unoccupied molecular orbitals (LUMOs) extend on the C-C bonds of *o*-carboranes in the cases

of ***o*-an**, ***o*-me-an** and ***o*-et-an** (Fig.S25). However, LUMO of **ph-*o*-an** completely concentrates on the *o*-carborane cage. Hence only CT transition is formed to produce the solely low energy CT emission. Besides, these *o*-carborane-based compounds show a higher luminous efficiency in toluene than that in THF (Fig.

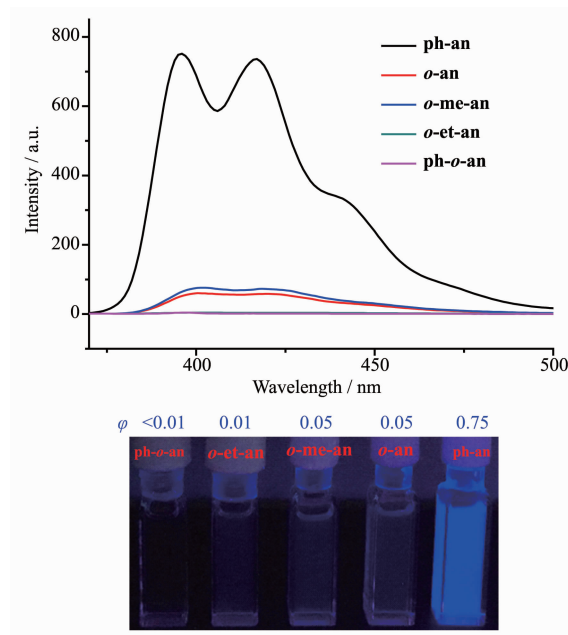


Fig.1 PL spectra (above) and luminescence photographs (below) of *o*-carborane-based luminophores in THF

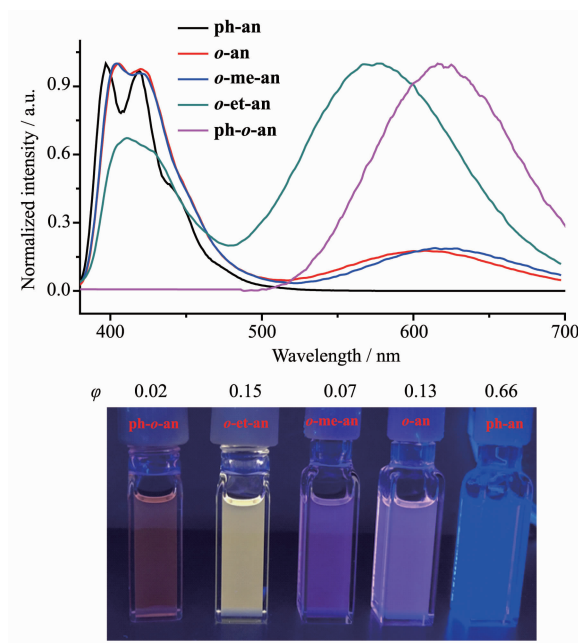


Fig.2 Normalized PL spectra (above) and luminescence photographs (below) of *o*-carborane-based luminophores in toluene

1 and 2), the same as the results previously reported^[38]. This could be interpreted that the C-C bond in *o*-carborane is sensitive to polarity of solvent. Increasing the polarity of solvent could induce enhanced C-C bond length variation^[39], further making the adverse effect to the luminous efficiency. Therefore, the C-C bond in *o*-carborane can be a lever to tune the excited state properties of chromophore, which serves as a non-radiative inducer for the excitons to decay.

2.2 AIE properties and X-ray analysis

To address whether this “flexible” C-C bond can lead to AIE properties, PL spectra in THF/H₂O with different water fractions were measured for all the compounds (Fig.S20~S23). In addition, to quantify the changes of emission efficiency in solution and in aggregate state, α value is defined as follows: $\alpha = \varphi_a / \varphi_s$, where φ_a and φ_s represent the aggregation- and solution-luminous intensity, respectively. Model compound **ph-an** shows evident ACQ phenomenon with a small α value: 0.14, suggesting the non-ignorable fluorescence quenching effect^[40] from the anthracenyl unit. However, those *o*-carborane-modified compounds exhibit totally

different emission behaviors. Typical AIE effect was found in ***o*-et-an** and **ph-*o*-an** with α values: 5.18 and 23.49, respectively. They were both virtually non-emissive in THF. As the fraction of water is increased (less than 70%), no notable enhancement was detected. However, a sharp intensified emission was observed when the fraction of water reached 70%. PL spectra of ***o*-et-an** reached its summit when the water fraction is 99% (Fig.3), whereas it is 80% in the case of **ph-*o*-an**. A further increase of water fraction to 90% leads to a decrease for **ph-*o*-an** in the emission intensity. Under this condition, **ph-*o*-an** might conglomerate into much larger particles and precipitate, thus causing the emission intensity to decline which is similar to the reported results^[41-43]. Thus, ***o*-et-an** and **ph-*o*-an** are AIE active. On the contrary, in the cases of ***o*-me-an** and ***o*-an**, ACQ effects were observed with α values: 0.60 and 0.80, respectively. Compound ***o*-me-an** shows emission in pure THF as strong as that observed in THF/water solution until the water fraction reaches 70% (Fig.3). Above this fraction, a dramatic decline in emission

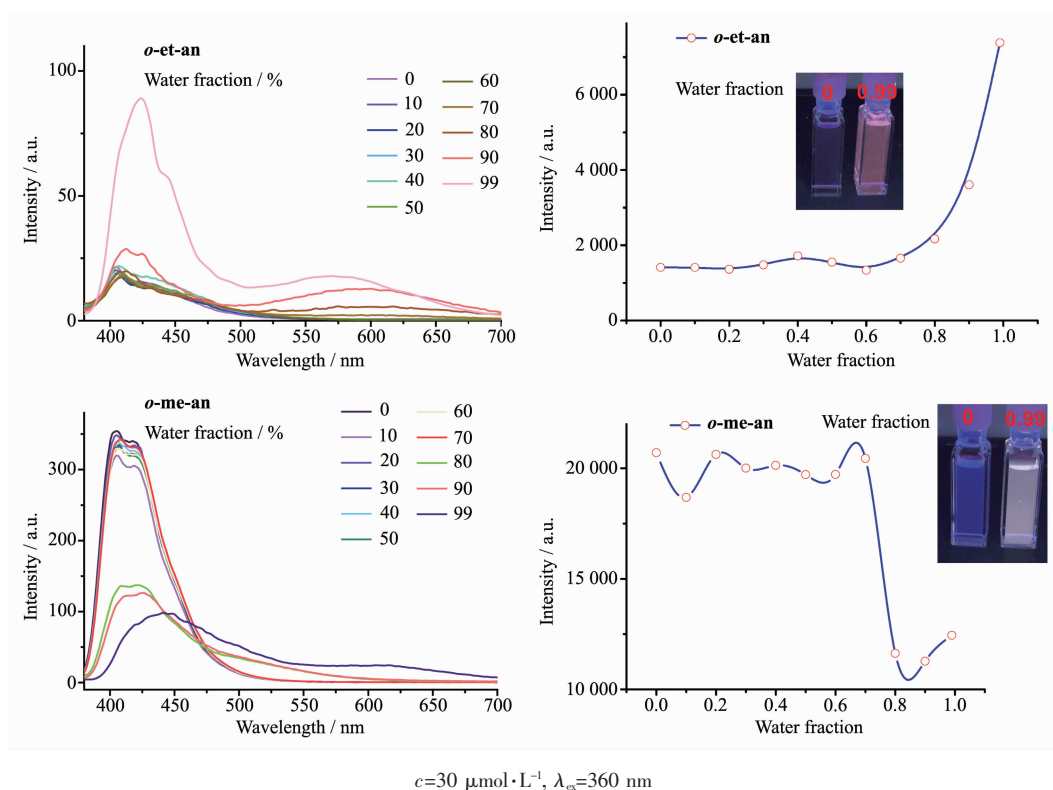


Fig.3 PL spectral changes of ***o*-et-an** and ***o*-me-an** in THF/H₂O with same concentration at room temperature

intensity was recorded. In addition, no apparent change in luminous intensity has occurred for ***o*-an**. Upon the water fraction up to 99%, low luminous intensity appears.

To unravel the roles that *o*-carborane has played, X-ray crystallographic analysis was carried out (Fig. S14). All the *o*-carborane-based luminophores display “face to face” (*o*-carborane to anthracene) packing patterns^[44] without $\pi \cdots \pi$ stacking interactions. With careful investigation, compound ***o*-an** shows strong $C_{\text{cage}}-\text{H} \cdots \pi$ interaction. Such intermolecular interac-

tions can't fully eliminate C-C bond vibration and rotation of *o*-carborane in solid state, even in the case of ***o*-me-an** where sterically hindered methyl group is attached to the benzene ring (Fig.4). On the other hand, the intermolecular $\text{B}-\text{H} \cdots \pi$ interaction was observed for compounds ***ph*-*o*-an** and ***o*-et-an** (Fig.4 and S14). Besides, the *o*-carborane substituents (ethyl or phenyl) can effectively suppress both the C-C bond vibration and the rotation of *o*-carborane to ensure rigid packing structures, thus leading to a profound AIE effect.

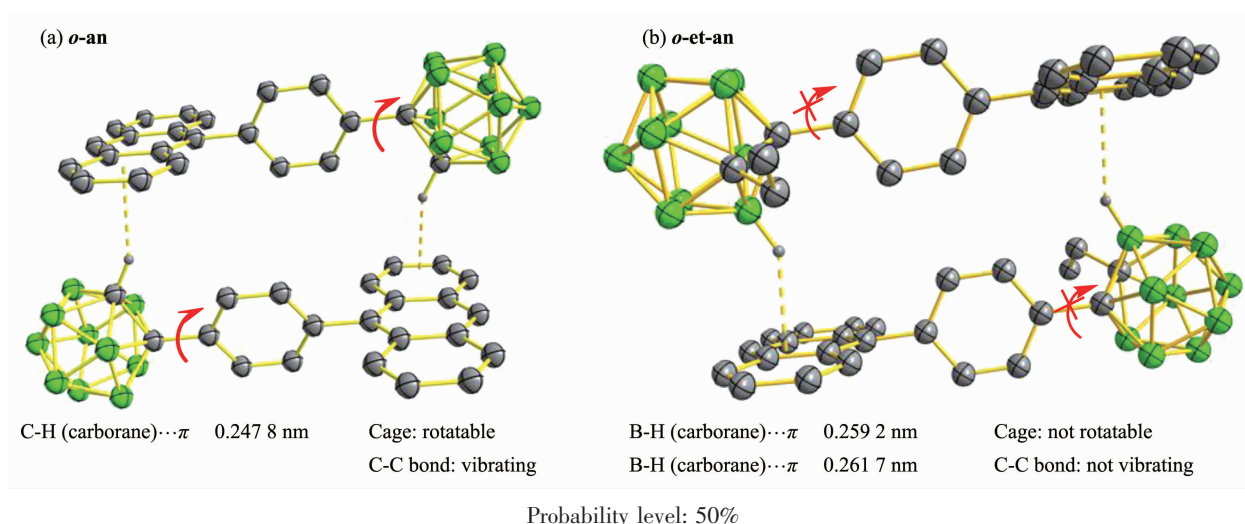


Fig.4 Crystal packing structures of ***o*-an** and ***o*-et-an**

3 Conclusions

In conclusion, our approach to realize ACQ luminophores to AIEgens transformation has been proposed by the engineering of variable C-C bond of *o*-carborane cores in the fluorescent molecules. A series of *o*-carborane-based anthracene derivatives were synthesized. Photophysical properties studies demonstrate the C-C bond vibration as a main non-radiative decay in solution. However, with physical constraints via intermolecular interactions in aggregate state, such non-radiative decay channel can be inhibited and lead to AIE phenomenon. Therefore, the variable C-C bond in *o*-carborane could be an effective tool to construct AIEgens, and some potential applications are in process based on these molecules.

Supporting information is available at <http://www.wjhxsb.cn>

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