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ARTICLE

Bromo induced reversible distinct color switching of a structurally simple donor-acceptor molecule by vapo, piezo and thermal stimuli

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Altering the luminescence properties of a material through external factors is an attractive feature that has the potential for various luminescence-related applications. Here, we report the synthesis and luminescence properties of two anthracene-based donor acceptor compounds, *N,N*-di-*p*-tolylanthracen-9-amine (TAA) and 10-bromo-*N,N*-di-*p*-tolylanthracen-9-amine (TAAB). In the solid state, the bromo-substituted compound TAAB shows reversible visible switching of the emission by external stimuli such as solvent, mechanical grinding and temperature. Single crystal X-ray studies, powder-XRD analysis and theoretical calculation reveal that the switchable emission is originated from the different stacking modes of TAAB. Furthermore, we have found that the bromo group interaction in the solid state plays a crucial role in this tunable emission. The other anthracene-based compound TAA does not show such switching of the emission by external stimuli. The observed changes of luminescence of TAAB by external stimuli suggest potential applications in rewritable optical media, sensors, and optoelectronic devices.

1 Introduction

Stimuli-responsive organic luminescent materials are of great importance due to diverse applications such as sensors, security inks, memories, displays, switches and organic light emitting diodes.¹ Great efforts have been devoted to the molecular design and modification to achieve color tuning and luminescent properties.² Reversible switching of luminescent properties of organic materials by controlling the molecular packing instead of chemical alteration is highly innovative and suitable for practical applications. Since luminescent properties of organic solids greatly depends on the molecular packing and intermolecular interaction,³ control of the molecular orientation and stacking mode of fluorophores by external stimuli is an effective way to tune the luminescent properties of organic materials. In this regard, luminescent materials which exhibit dynamically switchable solid state emission properties, when they are subjected to external stimuli such as light,⁴ mechanical force,⁵ vapour⁶ and temperature,⁷ have been reported.

In this context, the stimuli-responsive luminescent materials, donor (D)-acceptor (A) based system are highly desirable, if it can produce high-contrast fluorescence.^{8a-c} To date, anthracene-based stimuli-responsive D-A systems are rarely reported,^{8d-f} although anthracene derivatives are well-known luminescent materials, with wide applications in light-

emitting devices.^{9a,b} Hydrogen bonding, π - π stacking and their collective interactions are important intermolecular interactions for the construction of stimuli supramolecular systems.^{9b-d} To explore new system and new mechanism for tunable luminescence by various external factors with reversibility is still of great challenge for practical applications. Our continued interest to find out new non-covalent interaction in the molecular packing and emission properties promotes us to undertake the current research.^{1f,h} Herein, we report the synthesis of a multi-stimuli responsive luminescent material, 10-bromo-*N,N*-di-*p*-tolylanthracen-9-amine (TAAB), its emission properties and crystal packing. This luminescent material responds sensitively to vapo, piezo and temperature stimuli reversibly with drastic color changes. More interestingly, intermolecular interactions of C and H with Br play a crucial role in the tunable emission properties. These non-covalent interactions are confirmed by single crystal-XRD.

2 Results and discussion

2.1 Photophysical properties and solvatochromic effect

Structure of the molecules utilized in this study is shown in Fig. 1. *N,N*-di-*p*-tolylanthracen-9-amine (TAA) was synthesised in good yields from 9-bromoanthracene and ditolylamine using a

palladium tri-*tert*-butylphosphine complex as the catalyst. Bromination of TAA by *N*-bromosuccinimide (NBS) gave the final product TAAB in good yield (Fig. 1).¹⁰

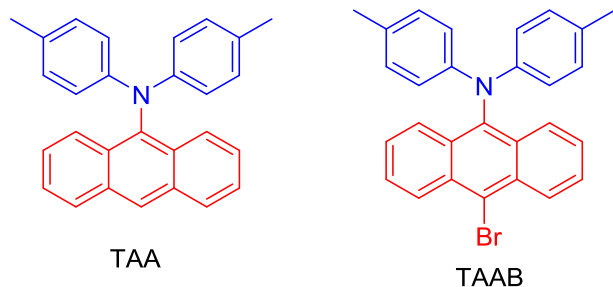


Fig. 1 Structure of TAA and TAAB.

The detailed synthetic procedures and characterization data are given in the experimental section and Supporting Information. As depicted in Fig. S1, the absorptions of TAA and TAAB in different solvents are nearly the same ($\lambda_{\max} \sim 440$ nm and 450 nm), but the emission of TAA shifts from 474 nm in *n*-hexane to 537 nm in DCM (Fig. 2a). Similarly the emission of TAAB shifts from 499 nm in *n*-hexane to 563 nm in DCM (Fig. 2b). The photographs of TAA and TAAB in various solvents under UV illumination are shown in Fig. 2c and 2d, respectively. The emission wavelengths strongly depend on the solvent used, revealing a bathochromic shift as the solvent polarity increases. Additionally, the fluorescence intensity is clearly reduced in high polar solvents. These results indicate that the TAAB emission is likely a charge transfer type.

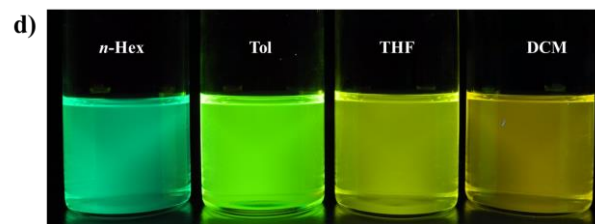
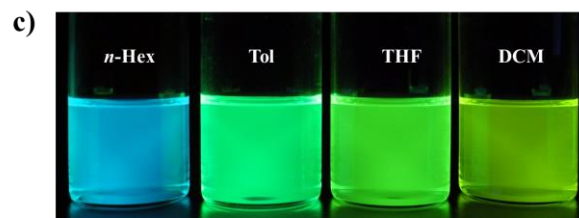
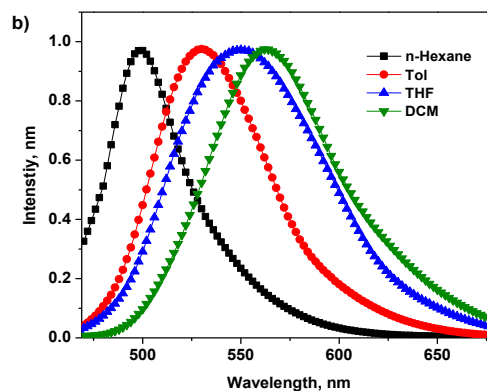
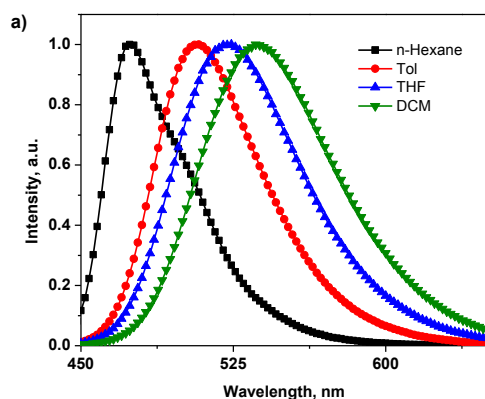


Fig. 2 Emission spectra of TAA (a) TAAB (b) in various solvents at RT (10^{-5} M), and photographs of TAA (c) and TAAB (d) in various solvents under UV irradiation.

2.2 Theoretical calculations

To gain insight into the electronic states of these two compounds, density functionalized theory (DFT) calculations were performed using Gaussian 03 program. Fig. 3a shows the electron cloud of the TAA and the result reveals that the highest occupied molecular orbital (HOMO) is mainly distributed on the electron donating tolylamine units and to a less extent on the anthracene group. On the other hand, the lowest unoccupied molecular orbital (LUMO) mostly spreads over the electron-accepting anthracene group. These results showed that TAA is a D–A dipole molecule with a strong charge transfer property from HOMO to LUMO in agreement with the observed solvent effect of the emission spectra. The HOMO and LUMO (Fig. 3b) of TAAB is similar to those of TAA. The HOMO is mainly distributed over the electron donating tolylamine unit and to a less extent on the bromoanthracene group and the LUMO mostly spreads over the electron-accepting bromoanthracene group.

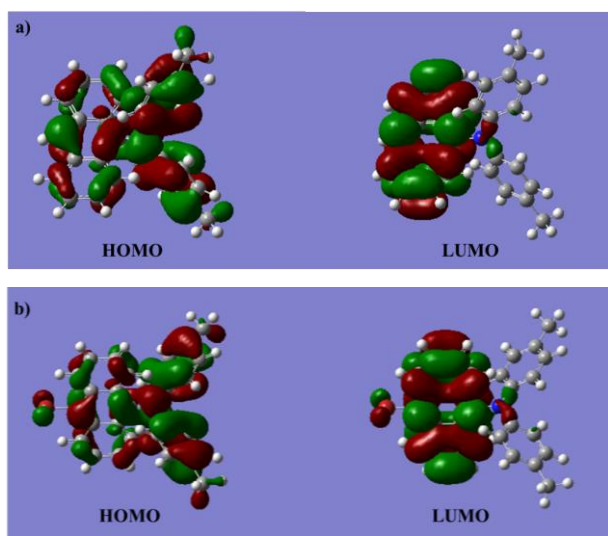


Fig. 3 Calculated electron contour plots a) HOMO and LUMO molecular orbitals of TAA, and b) HOMO and LUMO molecular orbitals of TAAB.

2.3 Molecular packing controlled emission

As shown in Fig. 4b, TAAB, upon crystallization from *n*-hexane, appears as red material under ambient light with a yellow orange luminescence at 577 nm under UV radiation (Fig. 4d) in contrast to the emission at 499 nm in the same solution. On the other hand, when the compound was crystallized from DCM or exposed to DCM vapour, the crystals show yellow color, giving green luminescence at 535 nm. A 42 nm hypsochromic shift from the yellow orange emission was observed (Fig. 4). Interestingly, the initial emission was recovered by heating the same at 70 °C. Such conversion between yellow orange and green emissions can be repeated many times without decreasing the intensity plausibly due to the non-destructive nature of the solvent stimuli. It is worth to note that the solid-state stimuli properties were not observed for TAA suggesting that the Br group plays a crucial role in the tunable emission properties of TAAB. The luminescent properties of molecules in the solid state, are known to be influenced by intermolecular interactions.¹¹ To understand the molecular packing and the intermolecular interactions of TAAB, single crystals grown from DCM and *n*-hexane were obtained by solvent evaporation. The crystalline structures were then determined by single-crystal X-ray diffraction analysis.

In *n*-hexane, TAAB was crystallized as monoclinic with each unit cell containing four TAAB molecules (Fig. S2). On the other hand, in DCM, TAAB was crystallized as orthorhombic with each unit cell containing eight TAAB and 8 DCM molecules (Fig. S2). The packings of TAAB crystals grown from different solvents are shown in Fig. 5. The crystals from *n*-hexane show that the molecules are lined up in a head-to-tail manner. As revealed in Fig. 5A, the Br group (head) interacts with the hydrogens and carbons on the two tolyl groups (tail) of the other molecule with interaction distances of 3.2–3.4 Å and 3.4–3.6 Å, respectively.

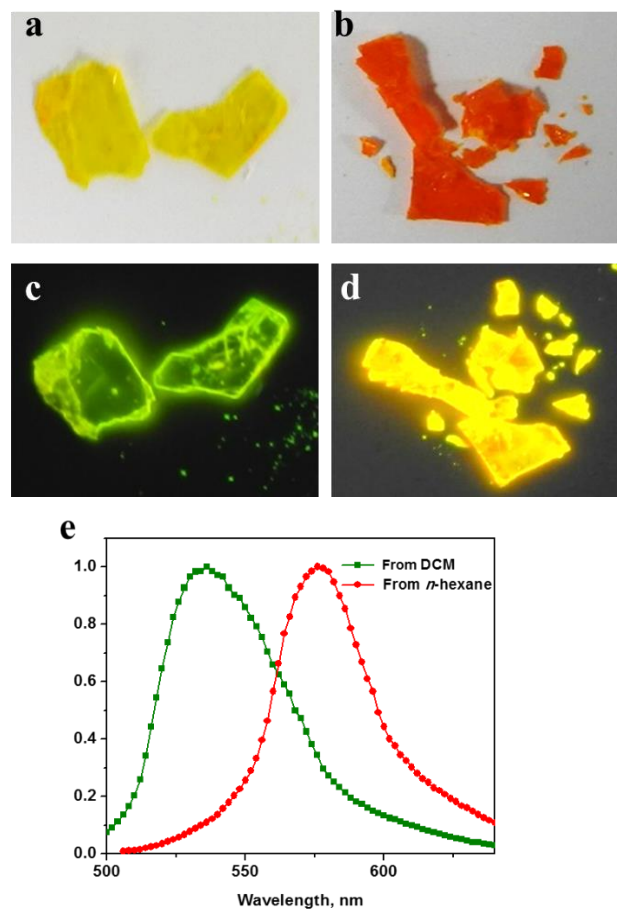


Fig. 4 Photographs of TAAB crystals: a) crystallized from DCM and b) from *n*-hexane under ambient light; c) from DCM and d) from *n*-hexane under UV-light; e) fluorescence spectra of TAAB crystals from *n*-hexane (red line) and dichloromethane (green line).

Since the Br group plays a crucial role in the emission properties, we performed the DFT calculations of two TAAB molecules with and without such interaction to see how strong this head to tail interaction is. The result shows that the interaction gives an energy decrease (stabilization) of 1.91 kcal/mole compared with the total energy of the two molecules without such interaction. The crystal packing further suggests there is no anthracene-anthracene interaction. However, the anthracene moieties show π - π and CH- π interactions with the tolyl groups of other molecules (Fig. 6). For the TAAB-DCM crystal, the anthracene groups are packed in a head-head manner. Each anthracene group overlaps with two other intermolecular anthracene groups via π - π stacking with the π -overlap area of about 1/4 (partial overlap) of an anthracene moiety and a distance of \sim 3.5 Å between the two overlapping anthracene planes.

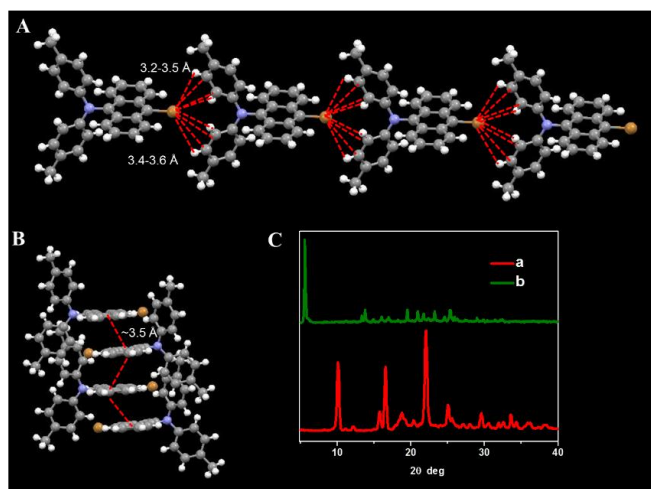


Fig. 5 Crystal packing of TAAB: A) crystallized from *n*-hexane; B) crystallized from DCM; C) the corresponding PXRD patterns of TAAB: a) crystallized from *n*-hexane and b) crystallized from DCM.

We also performed the DFT calculations of two TAAB molecules with an anthracene-anthracene π - π interaction shown in Fig. 5B. A stabilization energy of 0.95 kcal/mole was found for the interaction of two anthracene. The stabilization energies due to the intermolecular interactions and the resulted HOMO and LUMO levels in the TAAB crystals likely account for the distinct colors and emission wavelengths, although the details need more studies. To further evaluate the relationship between the vapochromism and the structures, we measured the powder X-ray diffraction (PXRD) patterns of the TAAB crystallized from *n*-hexane and from DCM. As shown in Fig. 5C, different PXRD patterns were obtained for these two samples. The observed patterns are consistent with the simulated powder patterns from the single crystal X-ray analysis of TAAB and TAAB-DCM (Fig. S3).

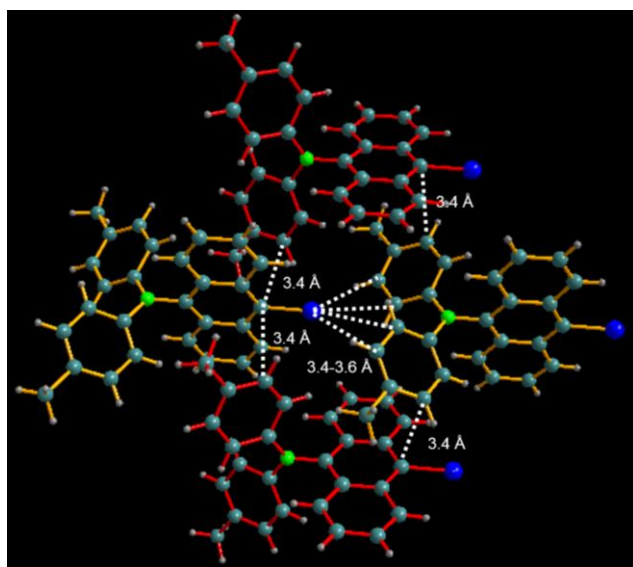


Fig. 6 Single crystal structure of TAAB crystallized from *n*-hexane (anthracene tolyl and Br- tolyl interaction).

2.4 Tunable emission upon external pressure

It is interesting to mention that TAAB exhibits piezochromism of the crystalline sample. When the material was ground in a mortar by a pestle, drastic color change from orange red to yellow orange was found (Fig. 7). This property appears reversible as indicated by the heat treatment at 140 °C for 10 min of the ground sample. Its emission color reverts back to that of the unground sample (Fig. S4). As indicated in Fig. 7, the emission maximum of TAAB at 577 nm was blue shifted to 543 nm after grinding. This is likely due to the fact that the intermolecular interactions (Fig. 5A and Fig. 6) were partially destroyed by the external pressure. It is noteworthy that grinding of crystals in many cases leads to red shift of the emission.¹² Conversely, TAA does not show significant luminance change under external pressure and this result further confirm the importance of bromo interaction in the piezochromism.

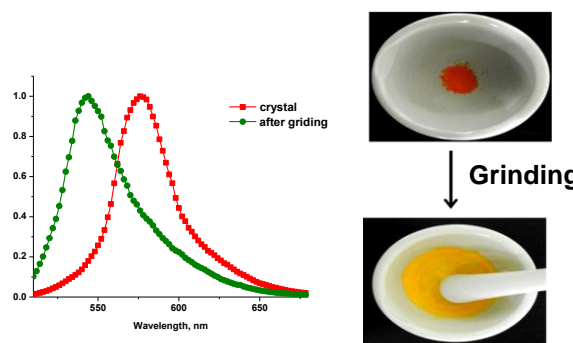


Fig. 7 a) Normalized emission spectra of TAAB before and after grinding, b) Photographs of TAAB under ambient light before and after grinding.

As shown in Fig. 5C-a, the PXRD pattern of TAAB shows intense and sharp peaks. In contrast, the ground sample of TAAB afforded very weak diffraction intensity (Fig. S5). The intensity decrease indicates that the grinding process converted the crystalline TAAB to an amorphous state.¹³ The observed small peaks in the PXRD pattern indicating that a small part of the crystalline sample remained after grinding. When the ground sample was heated at 140 °C for 10 min, the peaks in the PXRD pattern grew stronger. This result suggested that the amorphous ground sample could revert to the original crystalline state by heating. To demonstrate their utility for the practical application, a TAAB sample was taken into the mortar and was ground. The sample exhibited greenish-yellow emission under UV irradiation as shown in Fig. 8a. Letters 'C' and 'H' were written on the powder using DCM solvent to give green emission. The letters were erased upon heating the sample at 70 °C for 10 min and then grinding.

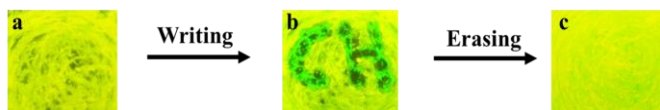


Fig. 8 Photoluminescence images of TAAB precipitated from *n*-hexane and ground in a mortar under UV irradiation at 365 nm. a) a ground sample; b) a sample after writing letters 'C' and 'H' with DCM solvent and c) the same sample after erasing the letters by heating at 70 °C for 10 min and grinding.

2.5 Temperature dependent fluorescence emission

Thermochromic photoluminescent materials in the solid state have received great attention due to the fact that photoluminescence is one of the most sensitive and easily detectable signals.^{7,14} However, in these cases, the thermochromism processes are sensitive to concentration and generally irreversible. Additionally, the fluorescent materials need to be doped in polymer along with a reference fluorescent material. To avoid these complications, a non-doped and highly luminescent material for the naked eye temperature indicator is highly desired. Here, we demonstrate that TAAB shows a reversible high contrast thermo responsive luminescence. When TAAB was cooled to 77 K, the initial orange red material turns to a yellow solid under ambient light and the yellow-orange emission at 577 nm shifted to a bright greenish-yellow band at 542 nm under UV irradiation. As shown in Fig. 9, the color change is visible to naked eyes. The color change is reversible, as the sample was warmed to room temperature, its color reverted back to orange red. This distinct reversible luminescence switching is very rarely observed in pure organic compounds in the solid state at low temperature.¹⁵ Further, to understand the sensitivity of the thermochromism, the time dependent fluorescence spectra were measured for various time intervals at 77 K and room temperature and were shown in Fig.10. The results suggest that the fluorescence switching is fast when the crystals were cooled to 77 K or warmed to RT.

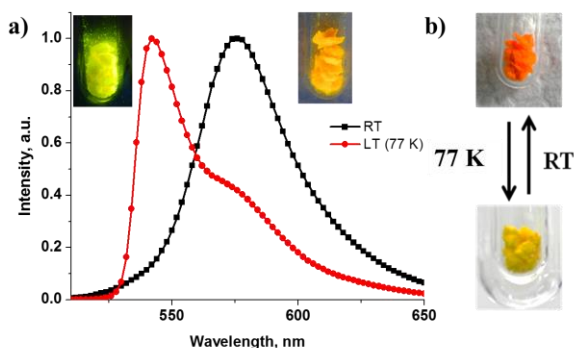


Fig. 9 a) PL spectra of TAAB at RT and 77 K (insets: the corresponding photographs under UV light), b) Photographs at room temperature and 77 K under ambient light.

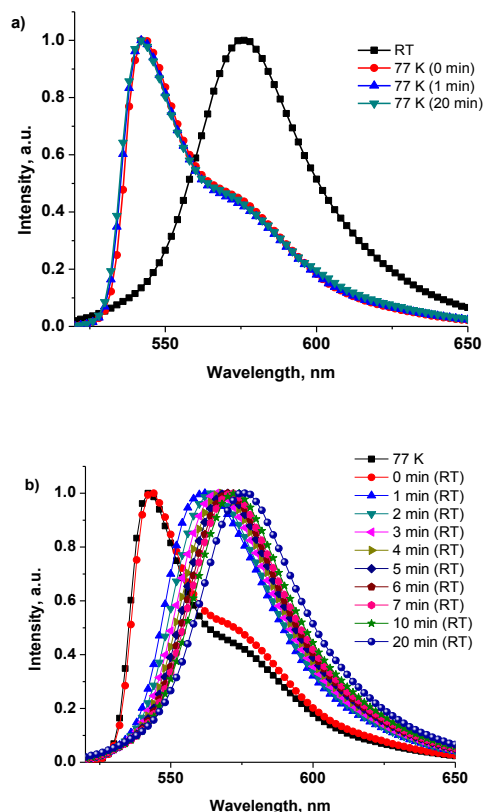


Fig.10 Fluorescence spectra of TAAB crystals after a) the crystals were cooled to 77 K; b) the crystals at 77 K were warmed in the air to room temperature for various time intervals.

3. Conclusion

We have synthesized an anthracene-based D-A system TAAB which exhibits multi-stimuli responsive luminescence including solvent, piezo and thermochromism with distinct color change. The crystalline sample of TAAB from *n*-hexane exhibited interesting vapochromism behaviors with emission colors changing from yellow orange to green, upon exposure to DCM solvents. Single crystal analysis and theoretical calculations of the TAAB-DCM crystal indicated that the hypsochromic emission is likely originated from the change in the molecular interaction of the TAAB molecules, change of Br-based interaction to anthracene-based one, leading to larger energy gap. Furthermore, emission color change was also observed upon grinding as well as cooling. It is noteworthy that this is a first example of a D-A compound which exhibits reversible multi-stimuli luminescence. The observed vapochromic, piezofluorochromic and thermochromic properties of this compound suggest potential applications in rewritable optical media, sensors, and optoelectronic devices. Comprehensive investigations in this direction is in progress in our laboratory.

4. Experimental section

4.1 General Information

Reagents and solvents were used as purchased without further purification unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded with a Varian Mercury 400 spectrometer. The HRMS spectra were recorded on a Finnigan MAT-95XL mass spectrometer. UV-vis spectra were recorded on a Hitachi U-3300 spectrophotometer and PL spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer. The molecular geometry optimizations and electronic properties were computed by carrying out the Gaussian 03 program with density functional theory (DFT) and time-dependent DFT (TDDFT) calculations, in which the Becke's three-parameter functional combined with Lee, Yang, and Parr's correlation functional (B3LYP) hybrid exchange-correlation functional with the 6-31G* basic set were used. The molecular orbitals were visualized on the Gaussview 4.1 software.

4.2 Synthesis of *N,N*-di-*p*-tolylantracene-9-amine (TAA):

A mixture of 9-bromoanthracene (5.00 g, 19.6 mmol), $\text{Pd}(\text{OAc})_2$ (43.0 mg, 0.19 mmol), tri-*tert*-butylphosphine (158.0 mg, 0.78 mmol), di-*p*-tolylamine (4.24 g, 21.6 mmol) and sodium *tert*-butoxide (3.10 g, 32 mmol) in dry *o*-xylene (40 mL) was placed in a sealed tube under a nitrogen atmosphere and was stirred at 120 °C for 15 h. After cooling, water was added to the reaction mixture and the mixture was then extracted with ethyl acetate. The organic layer was dried over anhydrous MgSO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatography eluted with *n*-hexane to give the desired yellow solid in 89% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.45 (s, 1H), 8.09 (d, 2H, $J = 8.8$ Hz), 8.02 (d, 2H, $J = 8.4$ Hz), 7.33-7.43 (m, 4H), 6.92 (s, 8H), 2.20 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 145.8, 137.8, 133.1, 131.04, 130.4, 129.9, 129.2, 126.8, 125.7, 124.8, 124.7, 120.3, 20.9; **HRMS** (EI^+) calcd for $\text{C}_{28}\text{H}_{23}\text{N}$ 373.1830, found 373.1833; **IR** (KBr): 3025, 2919, 2859, 1608, 1506, 1440, 1407, 1355, 1315, 1292, 811 and 734 cm^{-1} .

4.3 Synthesis of 10-bromo-*N,N*-di-*p*-tolylantracene-9-amine (TAAB):

TAA (5.00 g, 134 mmol) and *N*-bromosuccinimide (NBS) (2.86 g, 161 mmol) were dissolved in DMF: CHCl_3 (1:3, 60 mL) and the solution was stirred at room temperature for 6 h. After completion of reaction, water was added to the reaction mixture and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous MgSO_4 and evaporated under vacuum. The product was purified by silica gel column chromatography eluted with *n*-hexane. Red crystals of TAAB were obtained in 86% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.57 (d, 2H, $J = 8.4$ Hz), 8.13 (d, 2H, $J = 8.4$ Hz), 7.37-7.56 (m, 4H), 6.89-6.94 (m, 8H), 2.21 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 145.2, 138.1, 131.6, 131.5, 130.5, 129.7, 128.4, 127.2, 126.9, 124.9, 122.3, 120.0, 20.6; **HRMS** (EI^+) calcd for $\text{C}_{28}\text{H}_{22}\text{BrN}$ 451.0936, found 451.0935; **IR** (KBr): 3025, 2919, 2854, 1608, 1504, 1436, 1405, 1353, 1315, 1292, 809, 755 and 734 cm^{-1} .

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Notes and references

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† Electronic Supplementary Information (ESI) available: ^1H and ^{13}C spectra of 10-bromo-*N,N*-di-*p*-tolylantracene-9-amine, single crystal structure, photoluminescence spectrum and Powder-XRD. See DOI: 10.1039/b000000x/

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TOC graphics:

Bromo induced multiple distinct switching of emission of donor-acceptor molecule by solvent, external pressure and temperature

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Reversible distinct multiple switching of emission of a structurally simple donor-acceptor molecule TAAB in the solid state was achieved by external stimuli such as vapo, external pressure and temperature; the intermolecular interactions of C and H with Br group play crucial roles in this tunable emission system.