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New indole-containing luminophores: convenient synthesis and aggregation-induced emission enhancement

Qianqian Li[a], Shanshan Yu[a], Zhen Li[a]* and Jingui Qin[a]

A series of new indole-based luminophores (IIa–d) were conveniently synthesized through Ullmann reactions. They were well characterized by spectroscopic analyses and exhibited aggregation-induced emission enhancement (AIEE) properties. By simply changing the aromatic moieties in IIa–d, their maximum emission wavelengths could be well-tuned from 340 to 400 nm. The obtained experimental results, including the fluorescent behavior and the crystal structure in *solid*, demonstrated that the AIEE phenomena are caused by the restrictions of the intramolecular indolyl vibrational and rotational motions (around the Carbon–Nitrogen bonds). Copyright © 2008 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: indole; aggregation-induced emission enhancement; carbon–nitrogen bonds

INTRODUCTION

Organic luminophores have attracted increasing interest due to their potential applications as biological probes, chemical sensors, and organic light-emitting diodes, in the past decades. Thanks to the extensive efforts by many researchers, many kinds of luminophores with desirable properties have been developed.[1–15] However, to realize their practical utilization more comprehensively, some issues should be addressed. For example, organic luminophores generally exhibit strong luminescence in dilute solutions, however, in the solid state or in solutions with high concentration, the formation of delocalized excitons or excimers, due to the aggregation of the luminophores, often quenches their emission.[16–22] Thus, much effort has been applied to suppress the aggregation of organic luminophores.[23,24] In contrast to the normal thought of hampering the aggregation of luminophores, the best approach to the above notorious problem might be to develop new luminophoric materials whose aggregates could emit more efficiently than their solutions.[25–28] Along this line of approach, two novel photoluminescence (PL) processes have been identified: one is the 'aggregation-induced emission enhancement (AIEE)' and another is the 'aggregation-induced emission (AIE)'.[29–46] Siloles (TPS, Chart 1) are typical examples of AIE molecules, which were non-emissive in dilute solutions but highly emissive upon aggregation with the fluorescent quantum yields two orders of magnitude higher. As to the possible mechanism, the theoretical calculations, the experimental results obtained by a time-resolved fluorescence technique, and the *internal* structural control of silole examples, strongly supported the hypothesis that the AIE phenomena were due to the restrictions of the intramolecular phenyl vibrational and rotational motions (around the Carbon–Carbon bonds).[47–50] According to this point, some new AIE molecules were developed. For example, tetraphenylethene (TPE, Chart 1) and 4-*n*-butoxybiphenyl (BBP) were designed and demonstrated AIE properties.[51,52] As seen in Chart 1, in the AIE molecules, different π-construction blocks are linked together only through *Carbon–Carbon bonds*. The question can be posed: could other different linkage modes yield more AIE or AIEE molecules? If other linkage modes were possible, the family of molecules displaying AIE and AIEE will be expanded to a large degree.

In recent years, a series of AIE active molecules have been utilized as good bioprobes for protein, DNA, and even the formation of G-Quadruplex,[53–55] demonstrating the huge practical application of AIE (or AIEE) molecules in the field of biology. It is also envisaged that the AIE (or AIEE) molecules could be applied to detect some special biomacromolecules in live cell and perhaps, live organism selectively and sensitively. To realize this point, the AIE (or AIEE) molecules should be biocompatible, in addition to their good AIE (or AIEE) properties. Recently, we were interested in one heterocyclic moiety, indole, which is a very important constructing block in many naturally occurring compounds, and plays an important role in the fields of biochemistry and medicine (Chart 2). For example, indomethacin, the methylated indole derivative, is a non-steroidal anti-inflammatory drug commonly used to reduce fever, pain, stiffness, and swelling; indole-3-acetic acid, also known as IAA, is a member of the group of phytohormones called auxins, and is generally considered to be the most important native auxin; and L-tryptophan, an indole-containing amino acid, is used to

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* Correspondence to: Z. Li, Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan 430072, China.
E-mail: lizhen@whu.edu.cn

a Q. Li, S. Yu, Z. Li, J. Qin
Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan 430072, China

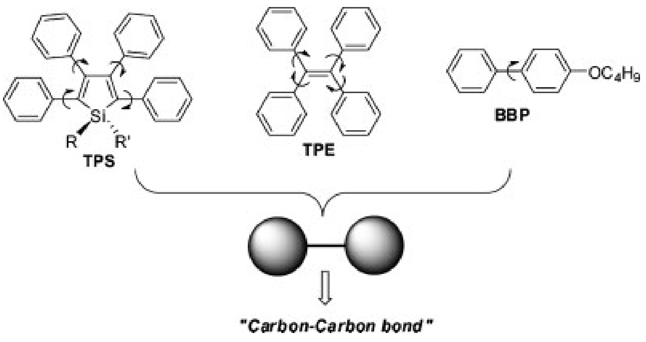


Chart 1.

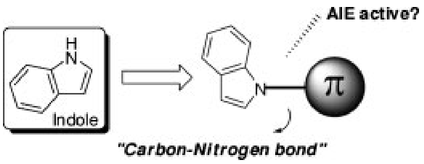


Chart 2.

alleviate depression, support alcohol withdrawal, and to aid weight loss. Thus, indole moieties should be biocompatible to live cells and the human body.[56–62] Considering this point, we wondered if it was possible to design some indole-based AIE active luminophores.

As mentioned above, the AIE (or AIEE) phenomena were derived from the restrictions of the intramolecular phenyl vibrational and rotational motions (around the Carbon–Carbon bonds). Accordingly and partially based on our previous work on indole moieties,[63–67] we would like to introduce some aromatic rings to indole groups through Carbon–Nitrogen bonds (the structure shown in Chart 2), and explore if it is possible to obtain new indole-based AIE (or AIEE) active molecules. Therefore, as shown in Scheme 1, four new indole-based compounds were prepared conveniently through the copper-catalyzed Ullmann amination reaction. The experimental results demonstrated that they were AIEE active luminophores, confirming that the linkage mode of Carbon–Nitrogen bonds could also work for the design of new AIE (or AIEE) active molecules. By changing the introduced aromatic moieties, the maximum emission wavelength of the resultant indole-based luminophores could be adjusted. Herein, we would like to present their syntheses, characterizations, and optical properties in detail.

EXPERIMENTAL SECTION

Materials and instrumentation

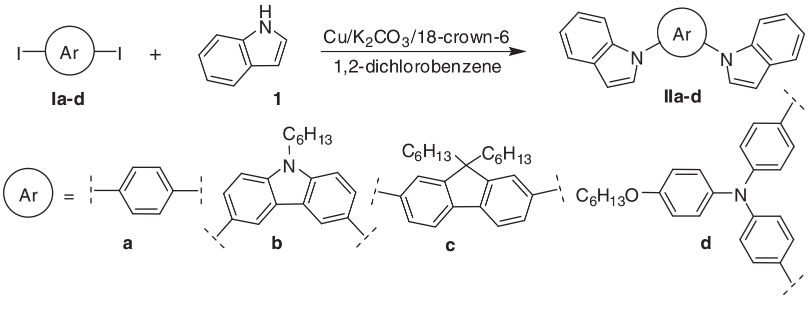
9-*n*-Hexyl-3,6-diiodocarbazole (**Ib**), 9,9-di-*n*-hexyl-2,7-diiodofluorene (**Ic**), and 4-(*n*-hexyloxy)-*N*,*N*-bis(4-iodophenyl)aniline (**Id**) were synthesized according to the literature methods. All other reagents were used as received. ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–4000 cm^{-1}. UV–Visible spectra were obtained using a Schimadzu UV-2550 spectrometer. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 °C min^{-1} in argon at a flow rate of 30 cm^3 min^{-1} for thermogravimetric analysis (TGA). Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. The thermometer for measurement of the melting point was uncorrected. Photoluminescence spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer. Single-crystal X-ray diffraction data were collected on a Bruker SMART diffractometer with an Apex CCD detector diffractometer using graphite-monochromatic Mo-Kα radiation at 293 K.

Synthesis of compound IIa

A mixture of indole (1.17 g, 10.0 mmol), 1,4-diiodobenzene (1.65 g, 5.00 mmol), copper powder (1.92 g, 30.0 mmol), potassium carbonate (6.90 g, 50.0 mmol), and 18-crown-6 (39.6 mg, 0.15 mmol) in 1,2-dichlorobenzene (20 ml) was heated at 180 °C for 48 h under an atmosphere of argon. After cooled to room temperature, the inorganic components were removed by filtration. The solvent was distilled under reduced pressure and the crude product was purified with column chromatography on silica gel using petroleum/ethyl acetate (20/1) as eluent to afford a white powder (500 mg, 32%). (Found: C, 85.01; H, 5.54; N, 8.75. $C_{22}H_{16}N_2$ requires C, 85.69; H, 5.23; N, 9.08%); ^{1}H NMR (300 MHz; CDCl$_3$; TMS) 7.73 (2H, d, *J* 7.5, ArH), 7.65 (6H, d, *J* 8.4, ArH), 7.41 (2H, d, *J* 2.7, ArH), 7.31–7.22 (4H, m, ArH), 6.75 (2H, d, *J* 3.0, ArH); ^{13}C NMR (300 MHz; CDCl$_3$; TMS): 138.2, 136.1, 129.6, 128.1, 125.6, 122.9, 121.5, 120.8, 110.7, 104.3; mp 217–219 °C; m/z (EI) 307.2 ($M^+ - 1$. $C_{22}H_{16}N_2$ requires 308.1).

Synthesis of compound IIb

A mixture of indole (1.17 g, 10.0 mmol), 3,6-diiodocarbazole (2.51 g, 5.00 mmol), copper powder (1.92 g, 30.0 mmol), potassium carbonate (6.90 g, 50.0 mmol), and 18-crown-6 (39.6 mg, 0.15 mmol) in 1,2-dichlorobenzene (20 ml) was heated at 180 °C for 48 h under an atmosphere of argon. After cooled to room temperature, the inorganic components were removed by



Scheme 1.

filtration. The solvent was distilled under reduced pressure and the crude product was purified with column chromatography on silica gel using petroleum/ethyl acetate (20/1) as eluent to afford a white powder (900 mg, 38%). (Found: C, 85.09; H, 5.95; N, 8.57. $C_{34}H_{31}N_3$ requires C, 84.79; H, 6.49; N, 8.72%); ^{1}H NMR (300 MHz; $CDCl_3$; TMS): 8.18 (2H, d, *J* 1.5, ArH), 7.73 (2H, d, *J* 6.6, ArH), 7.67–7.63 (2H, m, ArH), 7.58–7.54 (4H, m, ArH), 7.43 (2H, d, *J* 3.6, ArH), 7.26–7.16 (4H, m, ArH), 6.72 (2H, d, *J* 3.6, ArH), 4.43 (2H, t, *J* 7.2, N—CH_2), 1.99 (2H, m, CH_2), 1.49–1.32 (6H, m, CH_2), 0.92 (3H, t, *J* 7.5, CH_3); ^{13}C NMR (300 MHz; $CDCl_3$; TMS):139.9, 137.0, 132.1, 129.2, 124.0, 123.3, 122.4, 121.3, 120.4, 117.4, 110.7, 109.9, 103.1, 43.8, 31.9, 29.4, 27.3, 22.9, 14.4; mp 62–64 °C; m/z (EI) 481.5 (M^+. $C_{34}H_{31}N_3$ requires 481.3).

Synthesis of compound IIc

A mixture of indole (0.28 g, 2.40 mmol), 9,9-dihexyl-2,7-diiodofluorene (0.70 g, 1.20 mmol), copper powder (0.46 g, 7.20 mmol), potassium carbonate (1.66 g, 12.0 mmol), and 18-crown-6 (9.51 mg, 0.036 mmol) in 1,2-dichlorobenzene (5 ml) was heated at 180 °C for 48 h under an atmosphere of argon. After cooled to room temperature, the inorganic components were removed by filtration. The solvent was distilled under reduced pressure and the crude product was purified with column chromatography on silica gel using petroleum/ethyl acetate (20/1) as eluent to afford a colorless oil (450 mg, 67%). ^{1}H NMR (300 MHz; $CDCl_3$; TMS): 7.84 (2H, d, *J* 9.0, ArH), 7.72 (2H, d, *J* 7.5, ArH), 7.59 (2H, d, *J* 8.4, ArH), 7.50 (4H, br s, ArH), 7.43 (2H, br s, ArH), 7.25–7.19 (4H, m, ArH), 6.73 (2H, s, ArH), 2.02 (4H, br s, CH_2), 1.11 (12H, br s, CH_2), 0.78 (10H, br s, CH_2 and CH_3); ^{13}C NMR (300 MHz; $CDCl_3$; TMS): 151.4, 137.8, 137.6, 134.8, 128.3, 127.1, 122.3, 121.3, 120.2, 119.6, 119.3, 118.0, 109.5, 102.5, 54.5, 39.2, 30.5, 28.6, 22.9, 21.5, 13.0; m/z (EI) 564.3 (M^+. $C_{41}H_{44}N_2$ requires 564.4).

Synthesis of compound IId

A mixture of indole (1.10 g, 9.36 mmol), 4-(hexyloxy)-*N,N*-bis (4-iodophenyl) aniline (2.80 g, 4.68 mmol), copper powder (1.80 g, 28.1 mmol), potassium carbonate (6.46 g, 46.8 mmol), and 18-crown-6 (37.1 mg, 0.14 mmol) in 1,2-dichlorobenzene (19 ml) was heated at 180 °C for 48 h under an atmosphere of argon. After cooled to room temperature, the inorganic components were removed by filtration. The solvent was distilled under reduced pressure and the crude product was purified with column chromatography on silica gel using petroleum/ethyl acetate (20/1) as eluent to afford a white powder (1.4 g, 52%). (Found: C, 83.21; H, 6.22; N, 7.08. $C_{40}H_{37}N_3O$ requires C, 83.45; H, 6.48; N, 7.30%); ^{1}H NMR (300 MHz; $CDCl_3$; TMS): 7.69 (2H, d, *J* 8.4 Hz, ArH), 7.57 (2H, d, *J* 8.4, ArH), 7.37 (4H, d, *J* 8.7, ArH), 7.33 (2H, d, *J* 3.0, ArH), 7.26–7.16 (10H, m, ArH), 6.93 (2H, d, *J* 9.0, ArH), 6.67 (2H, d, *J* 3.0, ArH), 3.98 (2H, t, *J* 6.6, O—CH_2), 1.81 (2H, m, CH_2), 1.37–1.25 (6H, m, CH_2), 0.92 (3H, t, *J* 6.6, CH_3); ^{13}C NMR (300 MHz; $CDCl_3$; TMS): 156.6, 146.6, 140.1, 136.2, 134.0, 129.3, 128.3, 128.0, 125.6, 123.6, 122.5, 121.4, 120.4, 115.9, 110.8, 103.4, 68.5, 31.9, 29.6, 26.1, 22.9, 14.4; mp 123–125 °C; m/z (EI) 575.3 (M^+. $C_{40}H_{37}N_3O$ requires 575.3).

RESULTS AND DISCUSSION

Synthesis and structural characterization

As shown in Scheme 1, the four indole-based compounds (**IIa–d**) were easily prepared by the Ullmann reaction between indole and **Ia–d**, correspondingly. Indole was used directly without purification, and **Ia–d** were easily synthesized according to the similar procedure of Ullmann reactions reported in the literatures.[68,69] The yields were acceptable for Ullmann reactions.[70,71] It should be pointed out that the *meta* position to the nitrogen atom in the indole ring is very active, many substitutions could easily take place at this position. In **IIa–d**, these positions were left intact, thus some other functional groups could be substituted here to offer new functionality to these indole-based AIEE active molecules. For example, some hydrophilic groups could be introduced to enhance the solubility of the resultant molecules in water, leading to their possible utilization in live cells or the human body. This work is under way in our laboratory.

IIa–d were well characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, elemental analysis and EI-MS, and gave satisfactory data (Experimental section and Supporting Information). They were found to be thermally stable, with their TGA thermograms shown in Fig. S5. The 5% weight loss temperatures of **IIa**, **IIb**, and **IId** were 248, 365, and 363 °C, respectively. The good thermal stability would benefit their potential practical application.

Aggregation-induced emission enhancement (AIEE) properties and photophysics

All the obtained indole-based luminophores were soluble in common solvents, such as chloroform, acetone, ethanol, THF, acetonitrile, and dichloromethane. However, they demonstrated poor solubility in water. The UV–Vis absorption spectra are shown in Figs. S6–S14 with different concentrations. As the aromatic moieties between the two indolyl groups are different, **IIa–d** exhibited different absorption behavior.

IIa–d emitted detectable fluorescence upon excitation in dilute solutions. Figure 1 shows the fluorescent spectra of **IIa–d** in the THF solutions. The intensity was normalized for the comparison of their different maximum emission wavelengths. In **IIa**, two indolyl moieties are linked together by one phenyl group, and the maximum emission wavelength of this luminophore was observed at about 340 nm;.when the phenyl group was changed to a carbazolyl one in **IIb**, the wavelength was red-shifted to 360 nm. Similar phenomena were observed when fluorene and triphenylamino moieties were used in **IIc** and **IId**, respectively, with the maximum emission wavelengths at 392 and 400 nm, respectively. These results indicated that there are strong electronic interactions between the introduced aromatic rings and the two end-capped indolyl moieties through the Carbon–Nitrogen single bonds, to form an extended π system throughout the whole molecule. And by changing the aromatic group used, the maximum emission wavelength can be adjusted from ultraviolet region to the blue region of the visible spectrum. Thus, we can control the emission behavior of this kind of indole-based luminophore to some degree, as required for the potential applications, by simply introducing different aromatic moieties. Further work is in progress in our laboratory.

To determine whether the four indole-based luminophores were AIEE active or not, their fluorescence behavior was studied in mixture of THF and water of varying composition, since they could easily dissolve in THF but are insoluble in water (Figs. 2 and S15). Since the Φ_F values of **IIa–d** could not be accurately determined due to the involved technical difficulty, we thus plotted the changes in their PL peak intensities *versus* water content of the mixture (Fig. 2B). When the water fraction was increased from 0 to 50%, the fluorescence intensity of **IId** was enhanced correspondingly. This increase in fluorescence intensity can be attributed to an AIEE effect caused by the formation of

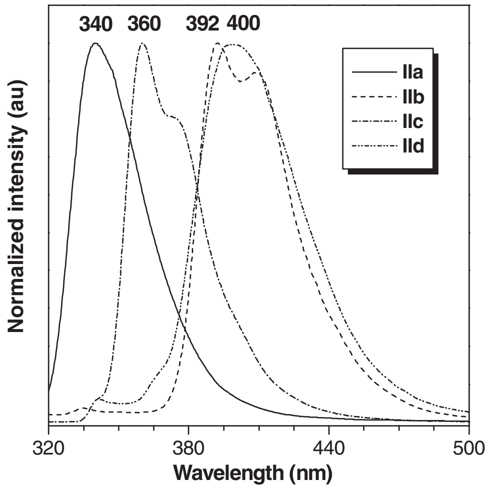


Figure 1. Normalized PL spectra of **IIa–d** in dilute THF solutions

molecular aggregates, in which restriction of intramolecular rotations (RIR) leads to increased fluorescent emission. However, further increase in the proportion of water in the solvent mixtures resulted in a decrease of the fluorescence intensity. We postulate that this phenomenon can be attributed to the decreasing number of emissive molecules located at the surface of the aggregates, relative to the non-emissive ones in their interiors, as the aggregates increase in size, upon increasing amounts of water being added to the mixtures. To support the above discussion and exclude the possible precipitation effect of **IId** in the mixed solvents, we tested its UV–Vis spectra in the mixed solvents. As shown in Fig. S16, in most cases, the absorption intensity are similar, indicating that there is no apparent precipitation effect present.

Similar phenomena were observed in the behavior of the other three indole-based molecules (Figs. 2B, and S17–S22). When a small amount of water was added to the THF solution of **IIa**, its emission intensity was increased immediately; it began to decrease when the water fraction was more than 50%. The fluorescent intensity of **IIc** reached a maximum at a water fraction of 60% in the solvent mixture. A similar trend was found for **IIb**. To exclude the possible influence from the organic solvent, two other solvents, DMF and ethanol, were used instead of THF (Figs. S23–S34). Similar results were obtained in the case of DMF: the fluorescence intensity was initially increased upon increasing the water fraction in the solvent mixture; however, it decreased when the water fraction in the solvent mixture was further increased (Figs. S23, S26, S29, and S32). These results confirmed that the AIEE properties of **IIa–d** are not dependent on the organic solvent. As shown in Figs. S24, S27, S30, and S33, when ethanol was used instead of THF and DMF mixtures, the fluorescent intensity of **IIa**–**c** decreased as the water fraction was increased in the solvent mixture. The phenomena could be due to the poor solubility of these luminophores in ethanol. This trend was not observed for **IId** which showed similar behavior to that observed in its THF and DMF mixtures, which can be attributed to the greater solubility of **IId** in ethanol mixtures.

As discussed above, in the mixture of organic solvent (THF, DMF, or ethanol) and water, only the molecules on the surface of the aggregates contributed to the detected fluorescence, many molecules inside would not be excited and thus emit fluorescence. Thus, in fact, the 'true' fluorescent intensity of **IIa–d** should be much higher than those recorded in the mixture solvent. In an attempt to observe the true fluorescence intensity of **IIa–d**, we doped them into poly(methylmethacrylate) (PMMA) with a concentration of 30%, then prepared thin films. As shown in Figs. S35 and S36, the fluorescence intensities of their films were much higher than those of the aggregation particles in the solvent mixtures. The maximum emission wavelength of the thin film of **IIa** was red-shifted by as much as 28 nm, indicating that there were some π–π interactions between different molecules in the solid state (we will discuss this later).

It is known that increasing the solvent viscosity can slow down intramolecular rotations[53–55] or strengthen the RIR process. We thus checked how variations in the viscosity would affect the emission. The fluorescence intensities of **IIa–d** were increased by adding glycerol, a viscous liquid, into their ethanol solutions (Figs. 3 and S37–S40). It was easily seen that the fluorescent intensities of **IIa**, **IIb**, and **IId** increased when the glycerol fraction was increased from 10 to 90%. The decrease of the fluorescence

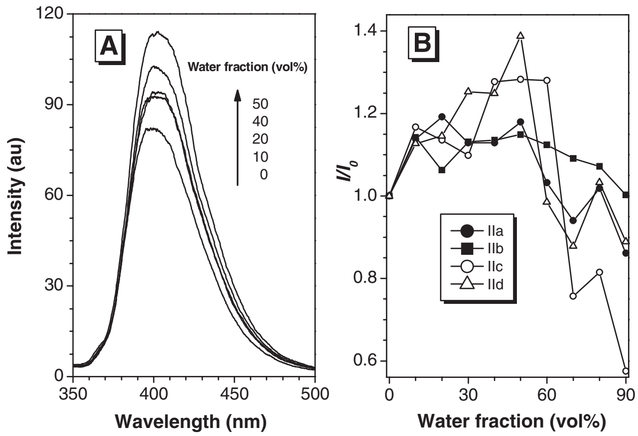


Figure 2. (A) PL spectra of the dilute solutions of **IId** in THF/water mixtures with different water fraction. Concentration: 1.0 μM. Excitation wavelength (nm): 329. (B) Changes in the PL peak intensities (*I*) of **IIa–d** with different water fractions in the THF/water mixtures. I_o = intensity in pure THF solution

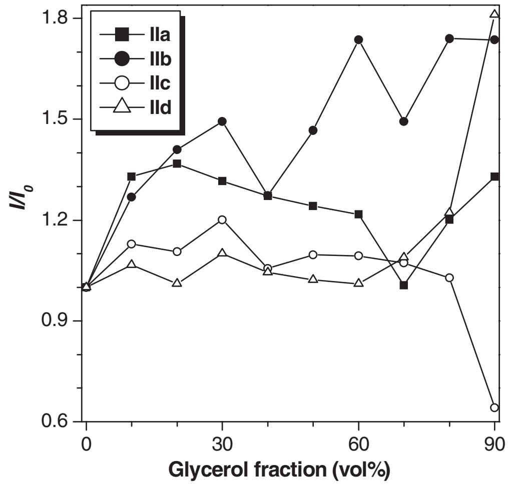


Figure 3. Changes in PL peak intensities (*I*) of the solutions of **IIa–d** with different glycerol fractions in glycerol/ethanol mixtures. I_o = intensity in pure ethanol solution. Concentration: 1.0 μM

intensity of **IIc** at high glycerol fraction should be ascribed to its low solubility in glycerol. Thus, the viscosity proved that **IIa–d** were AIEE active and the RIR process was indeed involved in the AIEE system. That was to say, the restriction of the rotation of the Carbon–Nitrogen bonds in **IIa–d** by the viscosity effect was responsible for the observed AIEE behavior.

Thus, the above experimental results demonstrate that the four indole-based dyes are AIEE active, confirming that the linkage of different π-construction blocks through Carbon–Nitrogen bonds could also yield AIE or AIEE molecules. Combined the fact that through Carbon–Carbon bonds, different π-construction blocks, as reported previously, could give AIE or AIEE dyes, it is expected that the linkage of different π-construction blocks together might result in AIE or AIEE luminophores, if the construction blocks could rotate around the linking bonds.

Crystal structure and molecular stacking feature

To obtain some information about the structure of the indole-based luminophores (**IIa–d**), we tried to grow single crystals of them. While our efforts in growing the crystals of **IIb** and **IId** failed, single crystals of **Ia** suitable for X-ray diffraction data collection were obtained by recrystallization from acetone solution (the Crystallographic data and refinement parameters can be found in the Supporting Information). In the crystal structure of **Ia**, the two indolyl groups and the benzene ring were not co-planar, but twisted by 51.1° (Fig. 4). This phenomenon is similar to those of 2,3,4,5-tetraphenylsiloles in solid state, [32] in which the aryl peripheries were all out of planarity with the silole core with typical dihedral angles of ~30° for the ring positions *ortho* to the silicon and larger twists of ~70° at the *meta* positions to the silicon atom. Thus, these facts indicated that the AIEE behavior of **IIa** was not due to the planarization of the molecule upon the formation of aggregate state, but the restrictions of the intramolecular phenyl vibrational and rotational motions (around Carbon–Nitrogen bonds). This point further confirmed that an alternative approach to the design of new AIE (or AIEE) luminophores is to utilize the linkage mode of Carbon–Nitrogen bonds, with comparison to the mode of Carbon–Carbon bonds as reported in most cases of AIE and AIEE luminophores. Therefore, encouraged by our examples and examples reported in the literature,[72] it can be assumed that many other AIE or AIEE luminophores could be designed through the linkage mode of Carbon–Nitrogen bonds.

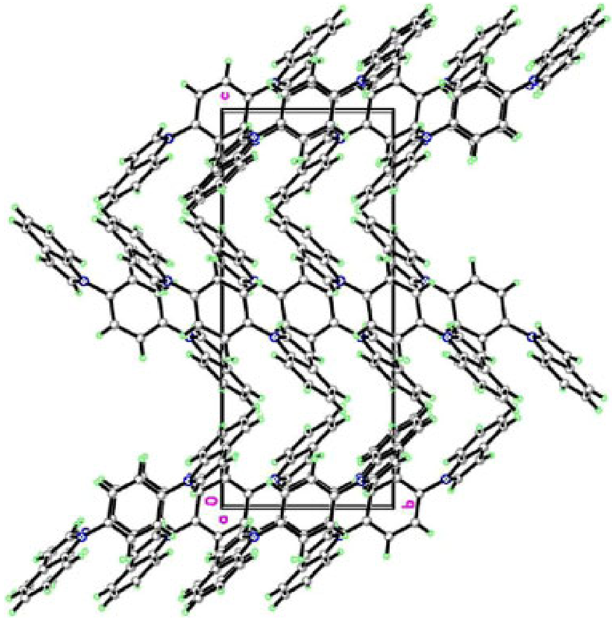


Figure 5. Packing diagram of **IIa**

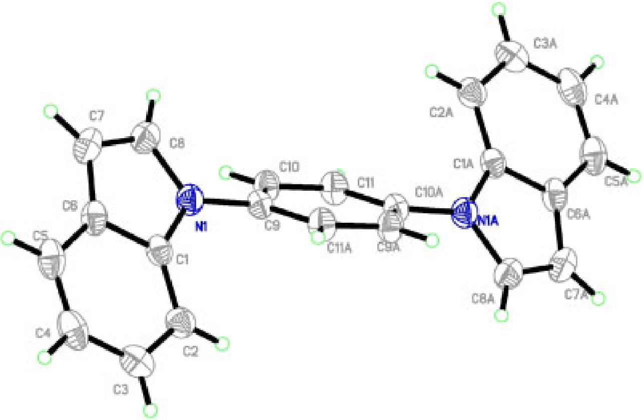


Figure 4. Molecular structure of **IIa**

Figure 5 shows a perspective view of the packing arrangements in the crystal of **IIa**. It is easily seen that there is some π–π stacking between different molecules. The indolyl rings are almost parallel, with adjacent indole moieties in two different molecules located at an average distance of 4.12 Å apart. Similar phenomena have been observed previously in the case of carbazolyl moieties.[51,52] This could also explain the phenomenon of the much red-shifted maximum emission wavelength of the thin film of **IIa** in PMMA, in comparison with that in dilute solution. In the cases of **IIb–d**, there was no large difference of the maximum emission wavelength between the thin films and solutions, thus, there is likely to be no or weak interactions between the indolyl groups of different molecules. This indicated that the changing of the aromatic rings linked to the indolyl group not only adjusts the maximum emission wavelength of the resultant luminophores, but also affects their packing model in the solid state. It would be useful to obtain the structures of **IIb** and **IId** for comparison.

CONCLUSIONS

With the aim to broaden the family of AIE and AIEE luminophores, a series of indole-based molecules were successfully and conveniently synthesized. All of them possessed good thermal stability and solubility, and demonstrated AIEE properties. By simply changing the aromatic groups between two indolyl rings, the maximum emission wavelength of the luminophores could be tuned from 340 to 400 nm. Thus, the linkage mode of different aromatic moieties through Carbon–Nitrogen bonds might be useful for the development of new AIE and AIEE luminophores. Coupled with their good biocompatible properties, the AIEE indole-based luminophores might find some practical applications in the field of biology.

Acknowledgements

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