

Fluorescence Spectroscopy |Hot Paper|

Rational Design of Dual-State Emission Luminogens with Solvatochromism by Combining a Partially Shared Donor–Acceptor Pattern and Twisted Structures

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Abstract: We report a general design strategy for a new class of luminogens with dual-state emission (DSEgens) that are brightly emissive in both the solution and solid state, with solvatochromism properties, by constructing a partially shared donor–acceptor pattern based on a twisted molecule. The DSEgens with bright fluorescence emission in both the solid and solution state demonstrate a unique solvatochromism behaviour depending on solvent polarity and thus may have applications in anti-counterfeiting.

The design and development of organic fluorescent materials have fundamental importance because these materials are widely used in various areas.^[1] Traditional dye molecules generally possess large conjugation, structural planarity, and conformational rigidity, thus exhibiting bright fluorescence in the dissolved state with disaggregation-induced emission (DIE) properties. These diverse dye molecules have long exploited proper functional design, but their utilization in the solid state has met great challenges because of their notorious aggregationinduced guenching (ACQ) behaviours.^[2] In contrast to traditional dyes (DIEgens), a new class of luminogens with aggregation-induced emission (AIE) has emerged.^[3] These AIEgens emit intense fluorescence in the aggregated or solid state, but become weakly emissive in the dissolved state. The specific AIE characteristic of AIEgens greatly promotes the advances of biosensing and organic optoelectronic systems.^[4] However, both DIEgens and AIEgens can only exhibit bright fluorescence in a single state (solution or solid state).

There is a growing interest in organic dual-state emission emitters (DSEgens), intensely emitting in both the solution and solid states, because these DSEgens fill the gap between ACQ and AIE. However, only a few examples demonstrated DSE be-

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haviours. One major strategy to design DSEgens is to add conjugation-induced rigidity in twisted molecules, for which conjugation-induced rigidity facilitates the emission in solution by suppressing intramolecular rotation and vibration, and twisted structures are used to avoid fluorescence quenching in the solid state caused by π - π stacking.^[5-9] Dual-state emission can also be attained by incorporating bulk substituents into molecular structures to prohibit π - π stacking in the solid state.^[10] A zero-twist donor-acceptor molecule was also found as a dualstate emitter,^[11] and a recent study showed that D- π -A structures can be used to achieve DSE properties.^[12] However, there is no valid design strategy for designing DSEgens with solvatochromism because of the lack of an investigation into the relationship between structure and DSE property.

Herein, we have designed and synthesized a group of dualstate emitters by combining the partially shared donor-acceptor pattern and twisted structures, and have investigated their dual-state emission behaviours and remarkable solvatochromism properties through experimental data and theoretical analysis. As shown in Scheme 1, rhodamine 6G as a representative of DIEgens only exhibit intense fluorescence in solution, whereas AIEgens such as tetraphenylethylene (TPE) merely emit intensely in the solid state. The designed products including 4-(N,N-diphenylamino)benzaldehyde (DPAB), 1-(4-(N,N-diphenylamino)phenyl)ethanone (DPPE), and (4-(N,N-diphenylamino)phenyl)(phenyl)methanone (DPPM) exhibit bright emission in both the solution and solid state, and this DSE phenomenon is markedly distinct from AIE and DIE. The twisted structure and a partially shared donor-acceptor pattern greatly contribute to the generation of dual-state emission. The distinct emission colours of these DSEgens in different solvents were explained with the aid of theoretical simulations, and their anti-counterfeiting applications were further demonstrated.

Three electron-withdrawing groups were introduced into a steric triphenylamine molecule, respectively, by Friedel Crafts acylation reactions (Scheme S1, Supporting Information). The obtained products were fully characterized using ¹H and ¹³C NMR and HRMS (Figures S1–S9, Supporting Information). Their UV/Vis spectra (Figure S10, Supporting Information) show that they have similar absorption patterns with two apparent absorption peaks at around 360 and 290 nm. Figure 1 displays PL spectra of the three compounds in THF solutions and in the solid state. The fluorescence emission maxima of DPAB, DPPE, and DPPM in THF are located at 492, 472, and 502 nm, respec-

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Scheme 1. Schematic illustration of distinct photophysical behaviours of three classes of luminogens: (a) Disaggregation-induced emission luminogens (DIEgens); (b) aggregation-induced emission luminogens (AIEgens); (c) dual-state emission luminogens (DSEgens).

2



Figure 1. (a) PL spectra of DPAB (50.0 μ M), DPPE (50.0 μ M), and DPPM (50.0 μ M) in THF. Inset: Fluorescent images. (b) PL spectra of DPAB, DPPE, and DPPM in the solid state. Inset: Fluorescent images.

tively, exhibiting intense green colours under the illumination of UV light. Their lifetimes are estimated to be 5.8, 5.6 and 5.4 ns from their respective time-resolved PL decay curve in Figure S11, Supporting Information, and such short emission durations in nanosecond magnitude clearly suggest their fluorescence nature from singlet states. It is interestingly found that the solids of all three compounds emit bright blue colours under the excitation of UV light, and their PL spectra in Figure 1b show that their emission peaks at 445, 433, and 450 nm are located at the blue light region, and their lifetimes fall in the range of 1.2–2.0 ns (Figure S12, Supporting Information), which are in the same order of magnitude with those in THF. Table S1, Supporting Information, summarizes photophysical properties of DPAB, DPPE and DPPM in THF and in the solid state, from which one can note that both solution and solid states for each of them possess high fluorescence quantum yields (\geq 15%), which definitively demonstrates that all the compounds have dual-state emission characteristics.

The large difference in emission maximum between solution and solid state for each of them implies the occurrence of a significant solvatochromism of fluorescence. As shown in Figure 2a, DPAB exhibits largely distinct fluorescence colours from blue to yellow depending on diverse solvents with different polarities. The emission maximum of DPAB in nonpolar toluene is located at 449 nm, but its emission peak is largely redshifted to 554 nm in polar acetonitrile. A gradual redshift of emission maximum, as the polarity of the solvent increases, is observed. Their lifetimes in diverse solvents fall in the range of 3.2-9.0 ns, and their emission efficiencies are all greater than 27% despite of varied PL intensity as shown in Figure 2b. Similar solvatochromism phenomena are also observed for DPPE and DPPM as shown in Figure S13–S14, Supporting Information, and all the photophysical properties of DPAB, DPPE, and DPPM in diverse solvents are summarized in Tables S2–S4, Supporting Information. These DSEgens have similar solvatochromism properties with common push-pull solvatochromic dyes like dansyl and prodan,^[13] but they show bright fluorescence in the solid state whereas those traditional solvatochromic dyes do not fluoresce in the solid or aggregated state. Differing from aggregation-induced emission enhancement of AlEgens, the PL intensities of DPAB, DPPE, and DPPM first abruptly decline

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Figure 2. (a) Normalized PL spectra and solvatochromism of DPAB (50.0 µм) in different solvents. (b) PL spectra of DPAB (50.0 µм) in different solvents.

and then gradually increase to the top as shown in Figures S15–S17, Supporting Information.

A twisted intramolecular charge transfer (TICT) mechanism may be responsible for solvatochromism behaviours of these DSEgens, similar to traditional TICT molecules for viscosity measurement.^[14,15] To verify this hypothesis, the PL spectra changes caused by the protonation and the following deprotonation of DPAB were recorded as shown in Figure S18, Supporting Information. The intense blue fluorescence of DPAB in toluene gradually declines with the addition of trifluoroacetic acid, but then progressively recovers following the introduction of excess triethylamine into the above system. These observations suggest that the bright-blue emission of DPAB in toluene originates from a TICT state because this emission can be greatly inhibited by the protonation of the triphenylamine moiety which converts the electron-donating triphenylamine to an electron-withdrawing triphenylaminonium ion. Similar results were also observed for DPPE and DPPM (Figures S19-S20, Supporting Information), which clearly demonstrates that the three compounds undergo a TICT emission. The solvent relaxation process of TICT fluorophores can be described by the Lippert-Mataga equation,^[16] and thus the dependence of Stokes shifts on the orientation polarizability (Δf) for the three compounds were evaluated as shown in Figure S21, Supporting Information. The increased Stokes shift along with the increase of Δf for each of them clearly suggests that they are all strong TICT fluorophores with highly localized excited-state charge separation. DFT calculations^[17] and natural bond orbital (NBO) analysis^[18] were performed to identify exact donor parts and acceptor parts for DPAB, DPPE, and DPPM. As shown in Figure 3, triphenylamine moieties dominantly contribute to the HOMOs of all three compounds, whereas the LUMOs mainly originate from carbonyl-containing phenyl groups, which indicate that the donors and acceptors share a phenyl ring for the three compounds. The charge-transfer process induced partially shared donor-acceptor pattern was also confirmed by their electron density difference maps (Figure S22, Supporting Information),^[19] which indicate that a major charge-transfer process occurs among the nitrogen atom, benzene moiety, and carbonyl group for each of them. As a result, a twisted intramolecular charge-transfer process induced by a partially overlapped donor-acceptor pattern in the molecules is responsible for intense fluorescence emissions for DPAB, DPPE, and DPPM in solvents.

A variable-temperature experiment on DPAB in THF was performed to explore the relation between structural conformation and emission location. Figure 4a shows that the emission maxima of DPAB are mainly located at around 460 nm when DPAB molecules are fixed in the solid THF at 77–170 K, but its



Figure 3. HOMOs and LUMOs of DPAB, DPPE, and DPPM calculated at the B3LYP/6-31+G(d,p) level.

Chem. Eur. J. **2019**, 25, 1–6

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3

These are not the final page numbers! **77**



Figure 4. (a) PL spectra of DPAB (50.0 μ M) in THF at different temperature from 77 K-270 K. (b) Optimized structures of DPAB at ground state and S1 state at PBE0/6-31+G(d,p) level. (c) Optimized structures of DPAB at S1 state in toluene and in acetonitrile at PBE0/6-31+G(d,p) level.

emission peak is largely red-shifted to 520 nm when DPAB molecules can freely rotate in liquid THF above 190 K, suggesting that the structural conformation of DPAB might dominantly determine its emission peak because its structure cannot be changed in solid THF but can be relaxed in liquid THF when it is excited. Thus, its structure at the ground state in THF was compared to that at the S₁ state from computations as shown in Figure 4b. It is apparently found that the dihedral angle $\theta_{C26-C24N12-C13}$ between one benzene ring linked to the nitrogen atom and the benzene ring linked to the carbonyl group at S₀ is greatly increased from 100.9° to 154.0° at S₁ state. These results prove that the emission location of DPAB is dominated by the relative position of the diphenylamino groups and the benzaldehyde moiety. To further verify this hypothesis, timedependent DFT (TDDFT) calculations^[20] on excited state structures and properties of DPAB in nonpolar toluene and in polar acetonitrile were performed. Figure 4c shows the optimized structures of DPAB at the S₁ state in toluene and acetonitrile. The formyl group is conjugated to the neighbouring benzene ring in the same plane for both the S₁ structures in toluene and in acetonitrile, but the relative position of the diphenylamino group to the benzaldehyde moiety in toluene is obviously different from that in acetonitrile because the dihedral angle $\theta_{C26-C24N12-C13}$ of the S₁ structure of DPAB is significantly increased from 96.5° in toluene to 103.9° in acetonitrile. Based on these S₁ structures, the calculated emission maxima of DPAB in toluene (481 nm) and in acetonitrile (571 nm) are very close to their corresponding experimental data in toluene (450 nm) and in acetonitrile (552 nm). The accordance between theoretical data and experimental data further substantiates the origin of solvatochromism for these D-A luminogens from subtle conformational changes caused by different solvents.

It is easy to imagine that twisted structures of DPAB, DPPE, and DPPM could overcome π - π stacking in the crystal or solid state. To confirm this hypothesis, their crystal structures determined by single-crystal X-ray diffraction were examined as shown in Figure S23, Supporting Information.^[21] It is readily found that all the three compounds exist in the twisted structure due to the distorted conformation of the triphenylamine moiety. The average intermolecular distances represented by the bond length of the N-N bond for the three compounds are greater than 5.0 Å, and the nearest C-C bond lengths are also longer than 3.7 Å, which clearly suggests that no significant intermolecular π - π interaction occurs for all the compounds. As a result, a twisted structure of the triphenlamine moiety mainly contributes to bright emission in solid state, while partially shared donor-acceptor pattern leads to a TICT state resulting in bright fluorescence in solution and significant solvachromism behaviour. The twisted structure and partially shared donor-acceptor pattern jointly results in dual-state emission and solvachromic properties of DPAB, DPPE, and DPPM. Their common DSE properties and solvatochromism behaviours suggest that such DSEgens can be designed by combining twisting structures and a partially shared donor-acceptor model.

The unique dual-state emission and solvatochromism properties of DSEgens in this work provide an opportunity for application in data encryption and anti-counterfeiting. Figure 5a



Figure 5. Data encryption demonstration of DSEgens using a number-based pattern (a) and anti-counterfeiting applications with DSEgens in a school badge (b) and a school motto in Chinese (c). The pattern a1 was covered with DPAB and TPE, and a2-a4 further were treated with toluene, THF and acetonitrile, respectively. The patterns in b1 and c1 were drawn with DPAB, and patterns in b2 and c2 were imaged after treating with THF.

Chem. Eur. J. 2019, 25, 1-6

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4

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demonstrates a simple example of the use of DSEgens in data encryption based on a number pattern. The pattern of the number "8" was first painted with a solution of tetraphenylethylene, and then part of the pattern was covered with a solution of DPAB. The pattern "8" in bright cyan colour can be observed under the UV light due to the solid-state emissions of TPE and DPAB, but the blue "8" can be changed to "6" in blue, green or yellow colour after spraying the pattern with toluene, THF or acetonitrile because of the disappearance of the blue emission from TPE in solution and specific solvatochromism behaviour of DPAB. The unique dual-emission properties of these DSEgens can also be expanded to anti-counterfeiting applications. Figure 5 b and c show a school badge and a school motto in Chinese drawn with a solution of DPAB on a paper. The bright cyan colour of the pattern and Chinese characters under the irradiation of UV light can be sharply turned to yellowish green after a simple treatment of THF, illustrating a great potential of these DSEgens with solvatochromism properties in anti-counterfeiting applications.

In summary, a new class of dual-state emitters with apparent solvatochromism was rationally designed by constructing a donor-acceptor pattern and by introducing a twisted triphenylamine moiety. A twisted intramolecular charge-transfer mechanism is responsible for their intense fluorescence, and the subtle conformational changes caused by different solvents during the excitation dominantly contribute to the unique solvatochromism behaviours of these DSEgens. Dualstate emission and solvatochromism of these D-A molecules were further used for anti-counterfeiting applications. This work clearly demonstrates a general design strategy for dualstate emission luminogens by the construction of a partially shared donor-acceptor pattern and the introduction of nonplanar structures, and also provides a rational explanation for the solvatochromism of these DSEgens.

Experimental Section

Experimental details are included in Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

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5



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Fluorescence Spectroscopy

Q. Qiu, P. Xu, Y. Zhu, J. Yu, M. Wei, W. Xi, H. Feng, J. Chen, Z. Qian*

Rational Design of Dual-State Emission Luminogens with Solvatochromism by Combining a Partially Shared Donor–Acceptor Pattern and Twisted Structures



Twisted chemistry! A general design strategy for a new class of luminogens with dual-state emission (DSE) and solvatochromism properties by constructing a partially shared donor-acceptor pattern based on a twisted molecule was reported (see figure).