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The Synergistic Effect between Triphenylpyrrole Isomers as Donors, Linking Groups and Acceptors on the Fluorescence Properties of D- π -A Compounds in the Solid State

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Abstract: Eight D-π-A compounds employing triphenylpyrrole isomers (TPP-1,2,5 and TPP-1,3,4) as donors, malononitrile (CN) and 1H-indene-1,3(2H)-dione (CO) as acceptors, pyridone (P) and benzopyran (B) as π-linking groups were synthesized. The compounds exhibited aggregation-induced emission and piezochromic properties. Compared with previously reported donors, triphenylpyrroles induced all the compounds to have more remarkable photophysical properties. The compounds containing TPP-1,2,5 and P moiety displayed stronger fluorescence intensities, shorter emission wavelengths, and more distinct piezochromic properties. However, the same phenomenon was observed in the TPP-1,3,4-containing system if B was as π -linker. Moreover, the CN acceptor endowed the compound to have a relatively strong fluorescent intensity, wherein CO induced a relatively long emission wavelength. That is, the photophysical properties of D-π-A compounds can be controlled through adjusting the structure of donor, linker and acceptor.

Introduction

Since Tang's group firstly discovered the aggregation-induced emission (AIE) phenomena in 2001,¹ compounds with luminescent properties have attracted considerable research interest in solid state or aggregate state because of their broad applications in high-tech fields, such as ion detection, in vitro and in vivo imaging, mechanosensors, and optoelectronic conversion.²⁻⁶ Among these materials, compounds with long emission wavelengths are of particular significance due to their great potential for practical applications.⁷ Basically, there are two fundamental ways to increase the emission wavelength of the molecule. One method is to enhance the conjugation degree of the molecules, which is beneficial to the electronic delocalization. However, a higher conjugation degree of molecule means a

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better molecular planarity, which tends to cause the molecules to accumulate in a face-to-face fashion in the solid state, thus resulting in strong intermolecular π - π interaction and aggregation-caused quenching (ACQ). Another method is to design a compound with a D- π -A structure, in which the intramolecular charge can be transferred from the donor to the acceptor (ICT).8 To date, most studies focus on this strategy because it can circumvent the issues of ACQ. Since there is lack of clear guidance and the appropriate donors, compounds with $D\text{-}\pi\text{-}A$ structures are rare and often have short emission wavelengths or weak fluorescence intensities. At present, the most commonly used electron donors are tetraphenylethylene,9-¹¹ triphenylamine,¹²⁻¹⁴ carbazole,¹⁵ thiazine,¹⁶ dimethylaniline,¹⁷ alkoxy,¹⁸ benzene,¹⁹ naphthalene,²⁰ anthracene,²¹ and so on. As some of these electron donors have relatively strong fluorescence intensities, D-π-A compounds containing these moieties have stronger fluorescence intensities. However, restricted by their limited electron-donating capabilities, these D- π -A compounds have relatively short emission wavelengths. On the other hand, another type of electron donors has strong electron-donating capabilities but have relatively simple structures, thus resulting in insufficient space among their twisted configurations. Therefore, the intermolecular interaction can not be effectively avoided when molecules are in the aggregate state, which causes a long emission wavelength but weak intensity. To solve this problem, many researchers combine these two kinds of donors in one compound. For example, a kind of D-π-A molecule consisting of triphenylamine and tetraphenylethylene as a co-donor²² was synthesized by Tang's group recently. It turned out that these two donors exactly complemented each other in terms of functions. Therefore, it is essential to design a donor with both strong electron-donating capability and highly twisted configuration.

More recently, we have synthesized two triphenylpyrrole isomers (TPP-1,2,5 and TPP-1,3,4) and demonstrated that these two compounds were not only capable donors but also had a highly decentralized spatial structure.²³ Moreover, TPP-1,3,4 was an AIE molecule because it had a greater space volume and more distorted molecular structure than TPP-1,2,5. with ACQ characteristic. Based on this previous result, we selected TPP-1,2,5 and TPP-1,3,4 to construct new D-π-A molecules. In the meantime, CN and CO were selected as acceptors. Since CO has a better conjugation than CN, COcontaining molecules tend to have a long emission wavelength.²⁴ In this work, the donor and acceptor are linked via an alkyl chain containing P (Pyridone derivative) or B (Benzopyran derivative). P linker has a highly twisted molecular structure, which is favorable for the target compound to have strong fluorescence intensity.24 On the other hand, the

conjugation of B linker is relatively high, which is advantageous for the material to have a long emission wavelength.²⁵ Based on this strategy, we designed and synthesized eight D- π -A compounds. Among them, four of them are P derivatives, and the others are B derivatives. All of them exhibited the aggregation-induced emission (AIE) properties, and most of them showed the piezochromic properties. The results of X-ray diffraction experiments revealed that the shift of the wavelength was attributed to the change in the molecular stacking mode, which means that the arrangement of molecules changed from order to disorder.^{26, 27} Overall, the comparison of these compounds indicated that compounds containing P linker had stronger luminous intensities while compounds having the B linker had longer wavelengths. More interesting, for the P-based compounds with the same acceptor, with the ones having the TPP-1,2,5 as the donor exhibited more stronger fluorescence intensity, shorter emission wavelength, and more distinct piezochromic properties than those having the TPP-1.3.4 as the donor. This result could be attributed to the fact that TPP-1.2.5 facilitates the orderly aggregation of molecules, thus leading to the P linked compounds have higher fluorescence intensities. In contrast, for B-based compounds, the same phenomenon was observed when TPP-1,3,4 as the donor. For the B-based compounds, TPP-1,3,4 is beneficial to avoid the interaction of molecules in the aggregation state due to a greater space volume and more distorted molecular structure of TPP-1,3,4. Moreover, precisely because the molecular conjugation is high, the B-based compounds have relatively long emission wavelengths. Furthermore, not only the donor would affect the fluorescence properties of the materials, but also the acceptor would also effect. The CN linker induces the derivative molecules to have a relatively dispersed spatial structure, which is favorable for the compounds to have stronger fluorescence. On the other hand, the CO linker increases the conjugation of the molecular, thus resulting in a longer wavelength.^{24, 25} Hence, we believe our work can considerably contribute to the designing of new AIE-compounds, to the understanding of the AIE phenomenon and mechanism, and to expanding the application fields of AIE-based materials.

Results and Discussion

Molecular structures and optical properties of target compounds

Chart 1 illustrates the molecular structures of the eight derivatives. The target compounds were prepared by the Knoevenagel condensation reactions starting from raw materials CN-P, CO-P, CN-B, CO-B, and TPP isomers in 40-75% yields. The molecular structures of all compounds were confirmed by NMR and MS. These compounds are soluble in common organic solvents, such as DMSO, CHCl₃, and THF, but insoluble in alcohol or water. Figure 1 displays the UV-vis absorption and emission spectra of these compounds in THF solution. The Pbased compounds (CN-P-1,2,5, CN-P-1,3,4, CO-P-1,2,5, CO-P-1,3,4) had three distinct bands in the range of 260-650 nm. The first band was in the visible area from 390 to 530 nm, which was attributed to the intramolecular charge transfer (ICT) from the TPP donor to CN or CO acceptor. It is noteworthy that CO has a better planarity, which increases the conjugation of the molecule and enhances the intramolecular charge transfer. As a result,

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Chart 1. Molecular structures of the compounds.

the bands of CO-P-1,2,5 and -1,3,4 were more intense than those of CN-P-1,2,5 and -1,3,4. The second band ranging from 310 to 390 nm could be ascribed to the localized π - π * transition. The last one ranging from 260 to 310 nm, could be regarded as the electronic absorption band of the TPP moiety.^{22, 28} The Bbased compounds, however, exhibited two absorption bands because the absorption band corresponding to the localized π - π^* transition was overlapped or not obvious. The band around 340-630 nm corresponding to the ICT from donors to acceptors, whereas another band was attributed to the absorption of the TPP moiety (Figure 1b).^{23, 24} Specially, the region corresponding to ICT in B-based compounds was broader, more intense and had longer absorption wavelengths than those of P-based compounds. This is because benzopyran ring with a better flatness and higher conjugation is more conducive to the flow of the electronic. For D- π -A molecules, when the intramolecular charge transfer effect is too intense, it will promote the red-shift of the wavelength and the widening of the corresponding absorption band, further causing the overlap with the second region that corresponds to the localized π - π * transition.^{11, 24}

Considering the push-pull electronic structure is helpful to enhance the ICT effect, we tested the UV-vis and fluorescence spectra of CN-P-1,3,4 and CN-B-1,3,4 in various solvents. As shown in Figure S1, the absorption spectra of CN-P-1,3,4 and CN-B-1,3,4 did not exhibited evident changes in different polar solvents. On the other hand, the FL spectra of CN-B-1,3,4 showed a certain degree of red shift from 566 to 594 nm with increasing solvent polarity from toluene to CH₃CN, showing a

strong solvatochromism effect. In contrast, the emissions of CN-P-1,3,4 only changed 7 nm almost without bathochromic shift. The influence of Δf on the Stokes shift (Δu) was further explored by the Lippert–Mataga equation in Figure 2 and Table S1^{29, 30}. For CN-B-1,3,4, it was found that the plot of Δu against Δf in these different polar solvents had a positive correlation with a slope of 221. However, for CN-P-1,3,4, there was no clear correlation between Δu and Δf . This indicated that B moiety has a more pronounced ICT effect, which further confirmed that B moiety possesses a higher molecular polarity (The dipole moments of CN-B-1,3,4 and CN-P-1,3,4 based on theoretical calculation were 11.8 db and 7.6 db, respectively).

As shown in Table 1, the four P-based compounds, CN-P-1,2,5, CN-P-1,3,4, CO-P-1,2,5, and CO-P-1,3,4, had emission peaks in the range from 550 to 563 nm in the THF solution, whereas the corresponding peaks of the B-based compounds were at 580–625 nm. Evidently, B-based compounds have longer emission wavelengths than those containing P moiety. In particularly, the large Stokes shifts confirm that the intramolecular charge transfer (ICT) in the excited states between the donor groups and acceptor groups could be stabilized in B-based compounds.

Though the fluorescence intensities of eight compounds were very weak in THF solution, the compounds in the solid state had the stronger fluorescence intensities, which showed a distinct AIE feature (Table 1). The time-resolved emission decay behaviors of the derivatives were studied, and their lifetime data are illustrated in Table 1. The lifetimes of B-based compounds and P-based compounds were 1.11-1.81 ns and 2.09-2.78 ns in the original solid state, respectively. From the data, it is clearly concluded that the fluorescence lifetimes of B-based compounds are relatively long, this may be related to the planar molecular configuration.^{31, 32} Meanwhile, B-based compounds in solid state have the longer emission wavelengths (604-686 nm) and lower fluorescent quantum yield (Φ_F = 5.4-15.2%) than those of Pbased compounds (λ_{em} = 585-611 nm and Φ_F = 15.0-22.1%), respectively. This could be attributed to the larger conjugation and the higher spatial planarity of the two connected bridges and donor groups in B-based compounds.^{23, 25, 26} It is well known that a better planarity of the molecule might dramatically promote the interaction between solid compounds. To avoid this kind of interaction, it can be achieved by adjusting the donor to make the whole molecule has a relatively dispersed spatial structure. Based on the previous introduction, we believed that could be





Figure 1. (a) UV-vis absorption and PL spectra of P-based compounds in THF (1×10^{-5} mol/L). (b) UV-vis absorption and PL spectra of B-based compounds in THF (1×10^{-5} mol/L).



Figure 2. The plot of Stokes shift (Δu) of CO-P-1,3,4 and CO-B-1,3,4 versus their Δf in solutions (Toluene, CHCl₃, THF, DCM, DMF, CH₃CN)

realized by TPP-1,3,4 unit as the donor. D-π-A structure constructed by TPP-1,3,4 and B moiety has a lower conjugation, which induces the shorter emission wavelengths of B-based compounds. In contrast, TPP-1,2,5 has a relatively small spatial structure and better planarity, which facilitates the orderly aggregation of molecules and causes the longer emission wavelength.23 For the P-based compounds, the molecular configuration of the pyridone bridge containing an alkyl chain is more twisted. More important, the molecule has a relatively large space volume because it has two donors. This structure has a fairly twisted spatial conformation, which can effectively suppress the interaction of molecules in the aggregation state. However, the arrangement of these large space volume compounds are often amorphous in the aggregate state, which is detrimental to the fluorescence properties of materials.33-35 Compared with CN group, CO group increases the conjugation of the whole molecule, thus resulting in a longer wavelength (Figure 3). Evidently, the results of this work will help the researchers to design new D-π-A compounds with AIE characteristics in the future.

Table 1. Photophysical properties of the eight derivatives.

Compounds	Abs/THF	Em/THF	Stoke's shift	Em/solid	$\Phi_{\rm F}/{\rm THF}$	Φ_F /solid	HOMO	LUMO	Eg	τ
	nm	nm	nm	nm	%	%	(eV)	(eV)	(eV)	(ns)
CN-P-1,2,5	303,347,426	550	124	585	1.0	22.1	-6.58	-1.29	5.28	1.81
CN-P-1,3,4	278,363,427	553	126	596	0.83	19.1	-6.61	-1.30	5.31	1.52
CO-P-1,2,5	296,360,453	561	108	597	0.92	17.8	-6.31	-1.12	5.20	1.11
CO-P-1,3,4	312,368,452	563	111	611	0.85	15.0	-6.37	-1.14	5.22	1.64
CN-B-1,2,5	291,424	582	158	616	0.34	9.3	-6.72	-1.80	4.93	2.27
CN-B-1,3,4	302,442	584	142	604	0.65	15.2	-6.88	-1.80	5.06	2.78
CO-B-1,2,5	286,488	620	132	686	0.21	5.4	-6.50	-1.58	4.93	2.53
CO-B-1,3,4	310,487	627	140	667	0.52	13.2	-6.75	-1.59	5.14	2.19

AIE properties of derivatives in aggregate state

As shown in Table 1, all compounds in this work had strong and distinct fluorescence in the solid (Φ_F were relatively high), however, weak or no fluorescence in the solution (Φ_F were very low), which indicated that these compounds had AIE characteristics. We systematically investigated their photophysical properties in the aggregate state and in solid. The UV-vis absorption spectra and PL spectra of two triphenylpyrrole isomers were measured in water-THF mixtures with different fractions of water, and their final concentrations were kept constant at 1 x10⁻⁵ mol/L according to the previous methods.

CO-P-1,2,5 emitted a weak vellow-green fluorescence at 561 nm in pure THF, which is caused by the free rotation of the phenyl ring and TPP ring via rotatable carbon-carbon single bonds and results in the consumption of energy in a nonradiative form.^{2, 36} When the fraction of water (f_w) in the THF-H₂O mixed solvent was below 40%, the PL intensity and wavelength of CO-P-1,2,5 were almost unchanged. With increasing of f_w from 50% to 90%, the PL intensity was enhanced about 15 times. Simultaneously, the emission wavelength was red-shifted from 560 to 608 nm. When f_w was further increased to 99%, the PL intensity of CO-P-1,2,5 slightly reduced. However, the emission wavelength continued to red-shift to 618 nm, which could be attributed to the high ratio of water. The solubility of the compound would be drastically reduced in the case of a high ratio of water, which leads to a relatively disorder intermolecular aggregation^{13, 37} (Figures 4a). The UV-vis absorption spectra of CO-P-1,2,5 in the THF/water mixtures solvent (1 × 10⁻⁵ mol/L) are shown in Figure S4. The absorption spectra were almost unchanged with increasing f_w from 10% to 40%. When f_w was increased to 50%, the entire absorption spectra exhibited a dramatic decrease and red-shift. Meanwhile, the absorption spectra of CO-P-1,2,5 contained light-scattering tails in the long wavelength region when the $f_w \ge 60\%$, indicating that CO-P-1,2,5 had clustered into nanoaggregates in the poor solvents. It was also found that the absorption spectra of CO-P-1,2,5 in the THF/water mixture with higher fw showed some differences in absorption band shapes and maxima, which might be considered to the formation of different nanoaggregate forms of molecules.^{29, 32} Dong, et al found that crystal-rich aggregation should be obtained in the middle range of water concentration. By increasing water contents, amorphous state should be dominant.^{38, 39} On the basis of these results, it is concluded that the fluorescence enhancement is attributed to the aggregation of



Figure 3. Fluorescence spectra of P (a) and B (b) solid samples

CO-P-1,2,5 induced by water, which blocks the non-radiative energy transfer and enhances the fluorescence emission of the CO-P-1,2,5 molecules. This result further confirms that CO-P-1,2,5 is AIE active. Similarly, CO-P-1,3,4 exhibited the similar changes in fluorescence intensity and emission wavelength when the water content was the same as that of CO-P-1,2,5, but the fluorescence enhancement (ca. 11 times, Figure 4b) was lower than that of CO-P-1,2,5, which was consistent with their

differences in fluorescent quantum efficiencies. These results indicated that the configurations of triphenylpyrrole isomers have different effects on the restriction of intramolecular rotation through changing the aggregation structure, leading to the differences in their fluorescent intensities.

For other derivatives, they also exhibited significant AIE properties. In general, as the fraction of water in water/THF mixture increased to about 50-60%, the fluorescence intensity gradually enhanced and reached the maximum value at about 90% of water fraction, and then declined to a certain extent with a red-shifting of the emission peak (Figure S3). Interestingly, the fluorescent enhancement ratios of the compounds containing TPP-1,2,5 donor were higher than those of compounds containing TPP-1,3,4 donor in aggregated state when pyridone ring was used as the π -linking group, no matter whether CN or CO was used as an acceptor. The fluorescent enhancement ratios of the compounds containing TPP-1,3,4 as donor were even higher if benzopyran mojety was used as a π -linking group. and consistent with their grind induced wavelength alteration (Figure 4c). In the aggregation state, chromophores would be surrounded by the hydrophobic molecules. It is likely that intermolecular interaction should also contribute to inducing the bathochromic shift. These comparison results are almost same as AIE quantum efficiencies of their corresponding compounds (Table 2), which reveals that the photophysical characteristics of derivatives in the aggregated state are determined by the synergistic effect of π -linking group and donor rather than by the type of acceptor. Based on our experimental data and the relative results in the literature, it is concluded that the construction of D-π-A compounds with AIE properties does not require an AIE molecule donor, but different donors have a significantly different effect on the optical properties of the compounds. To further study the mechanism of AIE formation, our lab is currently working on the development of single crystals.

Theoretical calculation

Density functional theory calculations were performed to reveal more information about the optical properties of D-π-A compounds at the molecular level by using a suite of Gaussian 09 program. The HOMO and LUMO energy levels of derivatives were calculated by using the TD-DFT with CAM-B3LYP method. Figure 5 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) charts of the derivatives CO-P-1,2,5, CO-P-1,3,4,CO-B-1,2,5, and CO-B-1,3,4.

The calculated energies (HOMO and LUMO) and band gaps (Eg) are listed in Table 1. Among eight D-π-A compounds, samples with TPP-1,2,5 donor showed higher HOMO energy. As can be seen from Figure 5 and Figure S2, the LUMO distributions of all the P-based compounds mainly lay on the pyridone ring and acceptor, and the HOMO distributions of the P-based compounds with TPP-1,2,5 donor mostly located on the TPP unit. Moreover, the HOMO distributions of compounds with TPP-1,3,4 donor mostly located on the entire molecule except for TPP unit, which is very different than compounds with the TPP-1,2,5 donor. However, the LUMO of all the B-based compounds almost delocalized to the whole molecule. The HOMO distributions of the compounds with the TPP-1,2,5 donor were also predominantly located on the TPP group, but the HOMO distributions of compounds with TPP-1,3,4 donor were much wider, including the C=C double bond located in the center



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Figure 4. (a) Fluorescence spectra of CO-P-1,2,5 (1 × 10⁻⁵ mol/L) in THE/water mixtures with different water volume fractions. (b) Eluorescence intensities and emission wavelengths of CO-P-1,2,5 and CO-P-1,3,4 versus the fraction of water (f_w) in THF/water (concentration 1×10^{-5} mol/L).(c) The highest fluorescence intensity ratio and wavelength alteration of all the derivatives (The order of the compounds was same as that listed in Table 1).

of the molecule. Apparently, their difference in HOMO distributions of compounds with different donors is relatively small. According to our previous work, compared with TPP-1,3,4, the TPP-1,2,5 molecule has a better planar configuration and lower dipole moments.²³ In combination with this theoretical calculation result, it can be concluded that the TPP-1,2,5 group has a stronger electron-donating ability than TPP-1,3,4. Meanwhile, this result also indicates that the B moiety facilitates the flow of electron cloud from the TPP unit to the donor core in the excited state.13

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Figure 5. Molecular orbital diagrams and energies for the LUMOs (left) and HOMOs (right) of the compounds CO-P-1,2,5, CO-P-1,3,4, CO-B-1,2,5, and CO-B-1,3,4 obtained from TD-DFT with CAM-B3LYP methods.

Piezochromic properties of the derivatives.

When the original samples were ground, the emission wavelength of the eight compounds showed a red-shift with different degrees because of their different acceptor, donor, and π -linker. The fluorescence images of all solid materials were captured under the 365 nm UV lamp. As shown in Figure 6a, after ground, the color of the sample (CO-P-1,2,5) changed from orange to bright red, which is a pronounced change. Correspondingly, the emission peak also red-shifted from 597 to 640 nm. When the ground sample was fumed by common organic solvent (e.g. CH₂Cl₂, CHCl₃, and THF), its color could be restored to the initial state, and the wavelength shifted back to 598 nm (Figure 7a). After the recovered sample was ground again, the luminous color and wavelength transformed significantly. Similarly, the sample ground in second time could also be recovered by solvent fuming. After several repeats, it fully demonstrated that the material had optimal reversibility and reusability (Figure 7b). It is noteworthy that the color change of the sample under the natural light could be distinguished by the naked eyes. As shown in Figure 6b, the color of the sample changed from yellow to orange. For the P-based compounds, the piezochromic properties (the alteration of wavelength and change of color) of compounds containing TPP-1,2,5 donor were more evident, which are unrelated to the acceptor type. The results are consistent with the AIE properties (Table 2, Figure S5, Figure S6). For the B-based compounds, all of them exhibited variation in the wavelength when stimulated by external pressure (Table 2, Figure S7), and CN-B-1,3,4 displayed the most significant color change among these four compounds (Figure S8). In particular, the compound with the TPP-1,3,4 donor was more favorable for the red-shift of the wavelength (Figure 4c), which is exactly the opposite of P-based compound

To investigate the mechanism of this piezochromic phenomenon, we carried out XRD measurements for the compounds in various states. The results showed both the diffraction peaks and dispersion peaks attributing to crystal state amorphous state, respectively, in all original compounds, indicating the coexistence of the crystal and amorphous state (Figure 8, S9 and S10). According to Figure 8a, the solid compound CO-P-1,2,5 in different states had different stacking modes. The diffraction curves of the original sample indicated many sharp and intense reflections due to being crystal-rich state. After being ground, the corresponding diffraction peaks were almost eliminated, suggesting the sample



Figure 6. (a) Fluorescence images of CO-P-1,2,5 solid samples taken under a 365 nm UV lamp. (b) Fluorescence images of CO-P-1,2,5 solid samples taken under a daylight lamp.



Figure 7. (a) Fluorescence spectra of CO-P-1,2,5 solid samples under various conditions. (b) Peak emission wavelength of CO-P-1,2,5 against number of grinding-fuming cycles

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was in an amorphous state at this time. However, after the ground sample was fumed with the organic solvent, the diffraction peaks were restored to the initial state, indicating the compound was recovered to the crystalline state. The results clearly demonstrated that the piezochromic properties should be attributed to the change in intermolecular arrangement pattern from the crystalline state to the amorphous state.⁴⁰⁻⁴⁵ Comparing the spectra before and after being ground, the absorbance wavelength and emission wavelength of the compounds in the amorphous state are longer than these in the crystalline state, which further proved the analysis (Figure S11).

For other P-based compounds, when CN-P-1,3,4 and CO-P-1,3,4 compounds were in the original state, their diffraction peaks were not very sharp, suggesting these compounds were not in good crystalline state (Figure 8b). After grinding, the change of intermolecular aggregation manner was not very significant (Figure S9). As a result, the variation in the fluorescent color was not very distinct. For the B-based compounds, when CN-B-1.3.4 and CO-B-1.3.4 compounds were stimulated by external pressure, the change of molecular aggregation form was relatively evident (Figure S10). However, only the CN-B-1.3.4 compound had distinct color change. The color change of CO-B-1.3.4 was not distinct because of its deep red fluorescence. The original samples of CN-B-1.2.5 and CO-B-1.2.5 were almost in the amorphous state, especially CO-B-1.2.5. Owing to the role of nitrile,24, 25 CN-B-1,2,5 compound had relatively twisted spatial structure. With external pressure, the intermolecular arrangement pattern changed slightly (Figure S10), which resulted in a slight variation in the wavelength and color. For CO-B-1,2,5, the intermolecular stacking modes hardly changed (Figure S10), correspondingly, the emission wavelength and the fluorescence color were almost unchanged. These results further elaborated that the donor has a significant influence on the spatial configuration of the molecule.

Conclusions

We designed and synthesized eight D-n-A compounds with two triphenylpyrrole (TPP) isomers (TPP-1,2,5 or TPP-1,3,4) as the donor, malononitrile (CN) or 1H-indene-1,3(2H)-dione (CO) as the acceptor, and pyridone or benzopyran as the π -linker. Compared with TPP-1,2,5 with ACQ characteristic, TPP-1,3,4 with AIE characteristic had greater space volume and more twisted molecular structure. Nevertheless, all eight compounds exhibited the aggregation-induced emission (AIE) properties and piezochromic properties. Moreover, all the compounds displayed longer emission wavelengths (the longest is 680 nm) and stronger fluorescence intensities (the highest Φ_F is 22.1%). More interesting, for P-based compounds with the TPP-1,2,5 as the donor exhibited more stronger fluorescence intensities, shorter emission wavelengths, and more distinct piezochromic properties, which is attributed to the fact that TPP-1,2,5 promotes the orderly intermolecular stacking. For B-based compounds with the TPP-1,3,4 exhibited the same phenomenon because TPP-1,3,4 suppresses the intermolecular interaction in the aggregation state. In addition, different acceptors also can affect the emission wavelength of the compounds. Specifically, malononitrile as a acceptor is favorable for the derivative to have a relatively strong fluorescence, whereas the 1H-indene-1,3(2H)-dione induces a relatively long emission wavelength.

Table 2. Emission wavelength of derivatives solid samples under various conditions.

		Alteration			
Sample	Original	Ground	Fumed	(nm)	
CN-P-1,2,5	585/22.1	619/13.8	587/20.8	34	
CN-P-1,3,4	596/19.1	617/14.6	595/18.3	21	
CO-P-1,2,5	597/17.8	640/9.9	596/17.1	43	
CO-P-1,3,4	611/15.0	628/9.1	613/13.9	17	
CN-B-1,2,5	616/9.3	630/5.8	619/9.6	14	
CN-B-1,3,4	604/15.2	637/8.2	602/14.3	34	
CO-B-1,2,5	686/5.4	692/5.1		6	
CO-B-1,3,4	666/13.2	681/7.5	665/12.4	15	



Figure 8. (a) XRD curves of CO-P-1,2,5 solid compound under different conditions. (b) XRD curves of four P-based compounds under original conditions

Experimental Section

Measurements and materials

All chemicals and solvents were commercially available and not further processed. 2-(1-butyl-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile (CN-P), 2-(1-butyl-2,6-dimethylpyridin-4(1H)-ylidene)-1H-indene-1,3(2H)-dione(CO-P), 2-(1-butyl-2,6-2-(2-methyl-4H-chromen-4-ylidene) malononitrile (CN-B) and 2-(2-methyl-4H-chromen-4-ylidene)-1H-indene-1,3(2H)-dione (CO-B) were obtained according to the synthetic methods

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reported in the previous literature.^{46,47} The structures of all products were confirmed by NMR and Mass Spectrum (MS). 1H spectra through a Bruker ARX400 spectrometer with CDCI3 as the solvent, and Mass Spectrum were performed by using a Finnigan BIFLEX III mass spectroscopy. The UV-vis absorption spectra were measured on a Persee TU-1901 UV-vis spectrophotometer. The Fluorescence spectra were determined on a Hitachi F-7000 spectrophotometer. XRD measurements were taken with a Bruker X-ray diffractometer (D8 Advance). Solid-state emission quantum yields (ΦF) were collected on a FluoroMax-4 (Horiba Jobin Yvon) fluorometer equipped contains an integrated sphere

The theoretical ground-state geometry and electronic structure of derivatives molecules were performed using the density functional theory (DT-DFT) with CAM- B3LYP hybrid functional at the basis set level of 6-31+G(d, p). All the theoretical calculations were optimized using Gaussian03 package.

Synthesis of PD: A mixture of TPP (1,2,5 or 1,3,4) (478.8 mg, 1.2 mmol), 2-(1-butyl-2,6-dimethylpyridin-4(1H)-ylidene)malononitrile (113.5 mg, 0.5 mmol), piperidine (0.5 mL), and DMSO (10 mL) was stirred under nitrogen for 48 h at 140 °C. After completion of the reaction, the mixture was cooled to room temperature, and then extracted with dichloromethane to remove DMSO. The organic layers were dried over anhydrous Mg₂SO₄. After removal of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethyl acetate) (5:1, v/v) to get pure compounds CN-P-1,2,5 or CN-P-1,3,4. The former is golden yellow solid (321 mg, 65%) and the latter is a yellow solid (361 mg, 73%).

The reaction of TPP (1,2,5 or 1,3,4) and 2-(1-butyl-2,6-dimethylpyridin-4(1H)-ylidene)-1H-indene-1,3(2H)-dione also used above method, And then get the target product CO-P-1,2,5 and CO-P-1,3,4. The first is a yellow solid (364 mg, 68%), And the second is an orange solid (396 mg, 74%).

CN-P-1,2,5: ¹H NMR (CDCl₃, 400 MHz): 7.42-7.65 (m, 17H), 7.04-7.26 (m, 25H), 6.51 (s, 4H), 3.99 (t, J = 8.0 Hz, 2H), 1.71-1.79 (m, 2H), 1.42-1.50 (m, 2H), 1.01 (t, J = 7.5 Hz, 3H). HRMS (EI) m/z calcd. For $C_{72}H_{55}N_{5}$, 989.45, found 990.42 [M⁺].

CN-P-1,3,4: ¹H NMR (CDCl₃, 400 MHz): 7.55-7.72 (m, 17H), 7.22-7.35 (m, 25H), 7.03 (d, 4H), 4.08 (t, J = 8.0 Hz, 2H), 1.80-1.88 (m, 2H), 1.45-1.51 (m, 2H), 1.04 (t, J = 7.5 Hz, 3H). HRMS (EI) m/z calcd. For $C_{72}H_{55}N_5$, 989.45, found 990.45 [M⁺].

CO-P-1,2,5: ¹H NMR (CDCl₃, 400 MHz): 9.04 (s, 2H), 7.36-7.63 (m, 18H), 7.04-7.26 (m, 26H), 6.52 (s, 4H), 4.14 (t, J = 8.0Hz, 2H), 1.78-1.85 (m, 2H), 1.38-1.47 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H). HRMS (EI) m/z calcd. C₇₈H₅₉N₃O₂, 1069.46, found 1070.45 [M⁺].

CO-P-1,3,4: ¹H NMR (CDCl₃, 400 MHz): 9.01 (s, 2H), 7.67-7.71 (m, 4H), 7.54-7.66 (m, 15H), 7.45-7.51 (m, 6H), 7.27-7.48 (m, 19H), 7.05 (d, 4H), 4.15 (t, J = 8.0Hz, 2H), 1.79-1.86 (m, 2H), 1.38-1.48 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H). HRMS (EI) m/z calcd. C₇₈H₅₉N₃O₂, 1069.46, found 1070.457 [M⁺].

Synthesis of BD: A mixture of TPP (1,2,5 or 1,3,4) (220 mg, 0.55 mmol), 2-(1-butyl-2,6-2-(2-methyl-4H-chromen-4-ylidene)malononitrile (104 mg, 0.5 mmol), piperidine (0.6 mL), acetic acid (0.3 mL), and toluene (15 mL) was refluxed under nitrogen for 18 h. After stopping the reaction, the solvent was removed directly under reduced pressure, then the crude product was purified by column chromatography (dichloromethane) to obtain pure samples CN-B-1,2,5 or CN-B-1,3,4. The first one is an orange solid (133 mg, 45%). The latter is a yellow solid (153 mg, 52%).

The reaction of TPP (1,2,5 or 1,3,4) and 2-(2-methyl-4H-chromen-4ylidene)-1H-indene-1,3(2H)-dione were carried out using the same experimental method, and then obtain the target compound CO-B-1,2,5 and CO-B-1,3,4. The former was a deep red solid (134 mg, 40%), And the latter was also a deep red solid (161 mg, 48%).

CN-B-1,2,5: ¹H NMR (CDCl₃, 400 MHz): 8.93 (dd, J = 8Hz, 1H), 7.44-7.77 (m, 10H), 7.12-7.26 (m, 12H), 6.83-6.89 (m, 2H), 6.51 (s, 2H). HRMS (EI) m/z calcd. C₄₂H₂₇N₃O, 589.22, found 590.22 [M⁺].

CN-B-1,3,4: ¹H NMR (CDCl₃, 400 MHz): 8.94 (d, J = 7.5Hz, 1H), 7.52-7.78 (m, 13H), 7.24-7.55 (m, 11H), 6.99 (d, 2H). HRMS (EI) m/z calcd. C₄₂H₂₇N₃O, 589.22, found 590.22 [M⁺].

CO-B-1,2,5: ¹H NMR (CDCl₃, 400 MHz): 8.71 (s, 1H), 7.43-7.86 (m, 14H), 6.98-7.26 (m, 14H), 6.51 (s, 2H). HRMS (EI) m/z calcd. $C_{48}H_{31}NO_3$, 669.23, found 670.24 [M⁺].

CO-B-1,3,4: ¹H NMR (CDCl₃, 400 MHz): 8.73 (s, 1H), 7.54-7.83 (m, 16H), 7.23-7.35 (m, 12H), 7.01 (d, 2H). HRMS (EI) m/z calcd. $C_{48}H_{31}NO_3$, 669.23, found 670.24 [M*].

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Keywords: D-π-A • Triphenylpyrrole Isomer donors • Piezochromic Properties • Aggregation-Induced Emission (AIE)

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The eight D-π-A compounds employing triphenylpyrrole isomers as donors, malononitrile (CN) and 1Hindene-1,3(2H)-dione (CO)as pyridone acceptors, (P) and benzopyran (B) as π-linking groups exhibit aggregation-induced emission properties evident (AIE) and piezochromic properties. The synergistic effect between donors, linking groups and acceptors on the fluorescence properties in the solid state may be clearly observed.

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Yunxiang Lei, Yueyin Lai, Lichao Dong, Guojun Shang, Jianbing Shi, Junge Zhi, Xiaobo Huang ,Bin Tong, Yuping Dong*

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The Synergistic Effect between Triphenylpyrrole Isomers as Donors, Linking Groups and Acceptors on the Fluorescence Properties of $D-\pi$ -A Compounds in the Solid State