

Unsymmetrical Triphenylamine–Cyanostilbene Donor–Acceptor Fluorophores: π -Spacer-Controlled Charge Transfer and Aggregation-Dependent Luminescence

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Abstract

The modulation of photophysical properties through π -spacer engineering represents an effective strategy for tailoring the performance of donor–acceptor fluorophores. In this work, two unsymmetrical triphenylamine–cyanostilbene conjugates, **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂**, were developed to elucidate the influence of phenyl and thiophene π -spacers on their electronic structures and emission characteristics. Both fluorophores exhibited efficient solution and solid-state luminescence; however, the incorporation of a thiophene spacer significantly strengthened the donor–acceptor interaction, resulting in a ~ 40 nm red shift in the absorption and emission maxima relative to the phenyl analogue. Quantum chemical calculations (DFT and TD-DFT) confirmed that the enhanced conjugation in **Th-TPA-(CN)₂** lowers the HOMO–LUMO energy gap and facilitates stronger intramolecular charge transfer (ICT). Although the phenyl derivative displayed a higher fluorescence quantum yield, the two compounds showed distinctly different aggregation-dependent emission behaviors. **Ph-TPA-(CN)₂** exhibited aggregation-caused quenching (ACQ), whereas **Th-TPA-(CN)₂** displayed aggregation-induced emission enhancement (AIEE), demonstrating that subtle variation of the π -spacer can switch the aggregation mechanism. This study establishes the crucial role of π -spacer selection in controlling charge-transfer interactions, emission color, and aggregation behavior, offering valuable molecular design principles for high-performance solid-state organic luminophores.

1.0 Introduction

Solid-state luminescent materials based on strategically coupled donor and acceptor motifs offer a versatile approach to controlling charge-transfer characteristics and excited-state dynamics, making them attractive candidates for advanced applications in optoelectronics^{1–4}, molecular sensing^{5–7}, photonics^{8–9}, and information-security technologies^{10–12}. Despite their potential, obtaining intense emission from organic molecules in the condensed phase is often difficult because molecular aggregation can induce unfavorable packing, strong chromophore–chromophore interactions, and reabsorption of emitted photons, collectively promoting non-radiative decay and suppressing the overall solid-state fluorescence^{13–14}. Consequently, the rational design of D–A systems capable of suppressing non-radiative decay while maintaining efficient radiative emission has become an important research focus. Among the various electron-donating building blocks, triphenylamine (TPA) has emerged as one of the most attractive donors because of its strong electron-donating ability, excellent hole-transport properties, and high thermal and electrochemical stability^{15–16}. More importantly, the propeller-shaped, non-planar geometry of TPA effectively suppresses detrimental π – π stacking in the solid state, thereby enhancing solid-state fluorescence¹⁷. Owing to these unique characteristics, TPA-based materials have found widespread applications in dye-sensitized solar cells (DSSCs)¹⁸, organic light-emitting diodes (OLEDs)¹⁹, organic field-effect transistors (OFETs)²⁰, nonlinear optical (NLO) materials²¹, and other organic electronic devices^{22–23}. Furthermore, structural modification of p-aryl-substituted TPA

derivatives provides an effective strategy for tuning the electronic structure, charge-transfer characteristics, and photophysical properties of these materials.

In contrast, cyanostilbene represents an effective electron-accepting motif owing to the strong electron-withdrawing character of the cyano group and its favorable solid-state emissive properties. Its integration with electron-rich donors enables the formation of donor–acceptor architectures with efficient intramolecular charge transfer (ICT), thereby offering tunable optical responses and enhanced luminescence^{24–25}. In addition, its rigid π -conjugated framework promotes favorable molecular packing, making cyanostilbene-based fluorophores attractive candidates for OLEDs, fluorescence sensors, and security applications^{26–28}. Nevertheless, cyanostilbene derivatives generally exhibit weak fluorescence in dilute solution because unrestricted intramolecular rotations and conformational relaxation provide efficient non-radiative decay pathways.

The combination of triphenylamine and cyanostilbene within a single molecular framework has therefore emerged as an effective strategy for developing highly emissive donor–acceptor fluorophores. Although several triphenylamine–cyanostilbene conjugates have been reported, most studies have primarily focused on modifying donor or acceptor substituents to regulate their optical properties²⁹. In contrast, the influence of the π -spacer connecting the donor and acceptor on the electronic communication, aggregation behavior, and solid-state emission has received comparatively less attention. Our research group has previously developed a series of carbazole–cyanostilbene donor–acceptor fluorophores, demonstrating that subtle structural modifications effectively regulate their solution and solid-state photophysical properties^{30–34}. Building on these findings, the present work explores the influence of replacing the carbazole donor with the stronger electron-donating triphenylamine unit and systematically investigates the effect of π -spacer engineering on the optical properties of unsymmetrical cyanostilbene fluorophores.

Accordingly, we designed and synthesized two novel unsymmetrical triphenylamine–cyanostilbene donor–acceptor conjugates, **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂**, incorporating phenyl and thiophene as the π -spacers, respectively. The introduction of different π -spacers enables systematic tuning of the electronic communication between the TPA donor and cyanostilbene acceptor, thereby influencing their solution- and solid-state photophysical properties. Both fluorophores exhibited bright fluorescence in solution and the solid state. Interestingly, **Ph-TPA-(CN)₂** displayed aggregation-caused quenching (ACQ) behavior, whereas **Th-TPA-(CN)₂** exhibited aggregation-induced emission enhancement (AIEE), demonstrating the decisive role of the π -spacer in controlling aggregation-dependent emission. Furthermore, **Ph-TPA-(CN)₂** emitted bright green fluorescence, while **Th-TPA-(CN)₂** exhibited yellow emission in the solid state with good fluorescence quantum yields. These findings highlight π -spacer engineering as an effective molecular design strategy for tuning intramolecular charge transfer, aggregation behavior, and solid-state emission in triphenylamine–cyanostilbene fluorophores, providing valuable guidelines for the development of advanced solid-state organic luminescent materials.

2.0 Results and discussion

2.1 Synthesis and characterisation

The synthetic strategy employed for the preparation of the target donor–acceptor conjugates is outlined in **Scheme 1**. The synthesis commenced with the selective mono-bromination of triphenylamine using N-bromosuccinimide (NBS) in dimethylformamide (DMF) at 0 °C, affording 4-bromotriphenylamine in moderate yield. The regioselective bromination provided a versatile synthetic intermediate for subsequent functionalization. The obtained monobrominated triphenylamine was then subjected to a Vilsmeier–Haack formylation reaction using a mixture of dry DMF and phosphorus oxychloride (POCl₃). This transformation selectively introduced a formyl group at the para position of the brominated phenyl ring, yielding 4-((4-bromophenyl)(phenyl)amino)benzaldehyde. Subsequently, 4-((4-bromophenyl)(phenyl)amino)benzaldehyde underwent a Miyaura borylation reaction with bis(pinacolato)diboron (B₂pin₂) in the presence of PdCl₂(PPh₃)₂ as the catalyst, producing the corresponding boronic ester intermediate (4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)benzaldehyde). The 4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)benzaldehyde was coupled with various aromatic aldehydes containing phenyl and thiophene moieties via Suzuki–Miyaura cross-coupling reactions, affording intermediates **1** and **2**, respectively. Finally, intermediates **1** and **2** were subjected to a Knoevenagel condensation with benzyl cyanide in methanol using sodium hydroxide as the base. This reaction furnished the desired cyanostilbene-based donor–acceptor conjugates (**Ph-TPA-(CN)2** and **Th-TPA-(CN)2**) in moderate to good yields. All newly synthesized intermediates and target compounds were comprehensively characterized using multinuclear nuclear magnetic resonance spectroscopy (¹H and ¹³C NMR) and high-resolution mass spectrometry (HRMS) (**Figure S1-S13**).

The spectral data were in good agreement with the proposed molecular structures. The successful formation of intermediates **1** and **2** was confirmed by their ¹H NMR spectra, which exhibited a characteristic aldehydic proton resonance at approximately δ 9.9–10.0 ppm. Upon Knoevenagel condensation, this aldehyde signal completely disappeared, indicating the consumption of the aldehyde precursor. Simultaneously, a new downfield resonance appeared at approximately δ 8.2–8.3 ppm, corresponding to the vinylic proton of the cyanostilbene framework. The appearance of this signal, together with the disappearance of the aldehydic proton resonance, provided clear evidence for the successful formation of the target compounds. Further structural confirmation was obtained from the ¹³C NMR spectra, which displayed characteristic signals corresponding to the nitrile carbon and the newly formed olefinic carbons of the cyanostilbene moiety. In addition, high-resolution electrospray ionization mass spectrometry (HRMS-ESI) revealed molecular ion peaks that matched the calculated molecular masses of the synthesized compounds, thereby unequivocally confirming their molecular compositions.

2.2 Photophysical Properties

The optical characteristics of the purified luminogens were initially assessed in DCM to establish the effect of the conjugated spacer on their electronic and excited-state properties. The absorption profiles revealed a clear spacer-dependent variation in the low-energy spectral region. **Ph-TPA-(CN)₂** showed an absorption maximum at 405 nm, whereas incorporation of the thiophene spacer in **Th-TPA-(CN)₂** shifted this band to 435 nm. These lower-energy features are assigned to the **ICT** transition between the donor and acceptor segments (**Figure 1** and **Figure S14**), indicating enhanced electronic communication upon introducing the thiophene unit. In addition, both compounds exhibited a strong high-energy absorption band near 230 nm, originating predominantly from the π - π^* transitions of the conjugated aromatic skeleton. The thiophene-containing derivative exhibits an approximately 30 nm bathochromic shift relative to its phenyl analogue, arising from the enhanced π -conjugation and stronger electron-donating character of the thiophene spacer³⁵ (**Table 1** (absorption and emission studies of target compounds)). These features promote greater electronic delocalization and reduce the HOMO–LUMO energy gap, resulting in a lower-energy transition consistent with reported thiophene-integrated donor–acceptor systems. The thiophene-containing derivative exhibits an approximately 30 nm bathochromic shift relative to its phenyl analogue, arising from the enhanced π -conjugation and stronger electron-donating character of the thiophene spacer. These features promote greater electronic delocalization and reduce the HOMO–LUMO energy gap, resulting in a lower-energy transition consistent with reported thiophene-integrated donor–acceptor systems. Cyanostilbene derivatives are generally known to exhibit relatively weak fluorescence in solution because of active intramolecular rotations and non-radiative relaxation pathways. Interestingly, the synthesized compounds displayed intense yellow color fluorescence with emission maxima centered at **550 nm** for **Ph-TPA-(CN)₂** and **585 nm** for **Th-TPA-(CN)₂**. The thiophene derivative exhibited a noticeable red-shift in emission, consistent with its extended conjugation and enhanced intramolecular charge transfer (ICT) character. The fluorescence quantum yields (Φ_f) were determined to be **0.31** for **Ph-TPA-(CN)₂** and **0.21** for **Th-TPA-(CN)₂**, indicating reasonably efficient emission in solution. The relatively high quantum yields, compared to conventional cyanostilbene analogues, can be attributed to the incorporation of the **triphenylamine (TPA)** donor unit, which not only enhances the electron-donating capability of the molecular framework but also contributes to a more rigid and conjugated architecture. The donor–acceptor interaction between the TPA moiety and the dicyanovinyl acceptor facilitates efficient radiative decay while maintaining favorable excited-state properties.

Table 1: Photophysical data of **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂** recorded in dichloromethane solution using UV–Vis absorption and fluorescence spectroscopy (λ_{ex} = 405 nm for **Ph-TPA-(CN)₂**; λ_{ex} = 440 nm for **Ph-TPA-(CN)₂**).

S. No	Compound	Absorption (nm)	Emission (nm)	Quantum Yields ^a
1	Ph-TPA-(CN)₂	405	520	0.31
2	Th-TPA-(CN)₂	440	555	0.21

Solvent Dependent studies

The solvatochromic behavior of **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂** was investigated in solvents of varying polarity, including hexane, toluene, diethyl ether, tetrahydrofuran (THF), dichloromethane (DCM), ethyl acetate, methanol, and acetonitrile, to evaluate the influence of the solvent environment on their electronic transitions and excited-state properties. The UV–Vis absorption spectra of both compounds exhibited an intense low-energy absorption band in the 400–430 nm region, which is attributed to the charge transfer (CT) transition from the electron-rich triphenylamine (TPA) donor to the electron-deficient cyanostilbene acceptor. This CT band was carefully monitored to examine the effect of solvent polarity on the absorption behavior. Only marginal changes in the absorption maxima and spectral profiles were observed with increasing solvent polarity, indicating weak solvatochromism in the absorption spectra. These results suggest that the ground state possesses a relatively low dipole moment and experiences minimal stabilization by solvents of different polarities. In contrast, the fluorescence spectra exhibited **pronounced positive solvatochromism**, demonstrating that the emissive excited state is considerably more polar than the ground state. As the solvent polarity increased from non-polar hexane to highly polar acetonitrile, both compounds displayed a gradual **bathochromic shift** in their emission maxima, accompanied by spectral broadening. Such behavior is characteristic of donor–acceptor systems possessing an **ICT excited state**, where polar solvents preferentially stabilize the charge-separated excited state, thereby lowering its energy. For **Ph-TPA-(CN)₂**, the emission maximum progressively shifted from **465 nm** in non-polar solvents to **600 nm** in polar solvents, indicating significant stabilization of the ICT excited state with increasing solvent polarity (**Figure 2, Figure S16 and Table S1-2** (Solvent dependence studies with different polarities of solvents)). The **Th-TPA-(CN)₂** derivative also exhibited similar solvatochromic response as compared with **Ph-TPA-(CN)₂**. The solvatochromic studies demonstrate that both **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂** possess strong ICT character in the excited state while exhibiting only weak solvent dependence in their ground-state absorption spectra. The marked positive solvatochromism observed in the emission spectra confirms the formation of a highly polarized excited state, highlighting the effectiveness of the donor–acceptor molecular design.

2.3 Aggregation induced emission enhancement (AIEE)

To investigate the aggregation-dependent emission behavior of **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂**, their photophysical properties were studied in acetonitrile (ACN)/water mixtures with varying water fractions. Acetonitrile serves as a good solvent for both compounds, whereas water acts as a poor solvent. Therefore, increasing the water content gradually, promoting molecular aggregation and enabling evaluation of their aggregation-induced emission enhancement (AIEE) or aggregation-caused quenching (ACQ) characteristics. Both compounds were readily soluble in pure ACN and exhibited bright fluorescence in solution. Upon gradual addition of water, aggregation of the molecules was induced, resulting in distinct changes in their emission intensity and spectral profiles. The aggregation behavior was evaluated by comparing the fluorescence intensity in pure ACN (0% water) with that obtained at high

water fractions (up to 90% water). For **Ph-TPA-(CN)₂**, a strong emission band centered at approximately 525 nm was observed in pure ACN. As the water fraction increased from 10% to 70%, the fluorescence intensity progressively decreased, accompanied by a slight bathochromic shift of the emission maximum to 560–580 nm. A further decrease in emission intensity was observed at 80–90% water, indicating that aggregation leads predominantly to fluorescence quenching rather than enhancement. This behavior is characteristic of aggregation-caused quenching (ACQ) (**Figure 3**). In contrast, **Th-TPA-(CN)₂** exhibited markedly different aggregation behavior. In pure ACN, the compound displayed a broad emission band in the 590 nm region. Unlike the phenyl analogue, the fluorescence intensity of **Th-TPA-(CN)₂** remained nearly constant up to a 70% water fraction. Upon further increasing the water content beyond 80%, the fluorescence intensity increased significantly, reaching its maximum at 90% water, indicating the onset of aggregation-induced emission enhancement (AIEE). The contrasting aggregation behavior of the two compounds originates from the nature of their π -spacers. In **Ph-TPA-(CN)₂**, the phenyl spacer promotes efficient π - π stacking in the aggregated state, leading to exciton quenching and enhanced non-radiative relaxation. Consequently, molecular aggregation suppresses fluorescence, resulting in typical ACQ behavior. In contrast, incorporation of the thiophene π -spacer increases molecular flexibility in solution while simultaneously providing a more twisted molecular geometry in the aggregated state. Upon aggregation, intramolecular rotations and vibrations are effectively restricted, thereby suppressing non-radiative decay pathways through the well-established restriction of intramolecular motion (RIM) mechanism. As a result, radiative decay becomes the dominant deactivation pathway, producing enhanced fluorescence intensity and typical AIEE behavior. These observations clearly demonstrate that π -spacer engineering plays a decisive role in regulating the aggregation-dependent emission properties of triphenylamine–cyanostilbene derivatives. Replacement of the phenyl spacer with a thiophene unit transforms the photophysical response from aggregation-caused quenching (ACQ) to aggregation-induced emission enhancement (AIEE). To gain further insight into the origin of the contrasting aggregation-dependent emission behavior, dynamic light scattering (DLS) measurements were performed to examine the size and characteristics of the aggregates formed in solution. Interestingly, the DLS analysis revealed a substantially larger hydrodynamic particle diameter for **Ph-TPA-(CN)₂** compared with its thiophene-containing analogue. The formation of larger aggregates in the case of **Ph-TPA-(CN)₂** suggests stronger intermolecular association and/or less favorable aggregate organization, which can facilitate close molecular contacts and enhanced intermolecular interactions. Such aggregation may promote excitonic coupling, π - π stacking, and other non-radiative deactivation pathways, thereby contributing to the observed fluorescence quenching in the aggregated state. In contrast, the smaller aggregate size observed for the thiophene-containing compound indicates a different mode of molecular organization. The incorporation of the thiophene spacer may introduce greater structural flexibility and alter the planarity and packing propensity of the conjugated framework, resulting in more loosely organized or differently packed aggregates (**Figure S20**). This molecular arrangement can suppress excessive intermolecular interactions while simultaneously restricting intramolecular motions, thereby favoring radiative decay and enhancing fluorescence upon aggregation. Thus, the DLS results provide supportive evidence that the nature of the π -spacer strongly influences

aggregate size and molecular packing, which in turn governs the transition between ACQ and AIEE behavior.

2.4 Solid State Emission Studies

Cyanostilbene derivatives are well known for their excellent solid-state luminescence, arising from the restriction of intramolecular motion and favorable molecular packing in the solid state. To evaluate the influence of the π -spacer on the solid-state emission properties, the photophysical behavior of **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂** was investigated by recording their solid-state photoluminescence (PL) spectra and fluorescence quantum yields. The **Ph-TPA-(CN)₂** derivative exhibited an intense yellow emission centered at approximately **560 nm**, with a solid-state fluorescence quantum yield (Φ_f) of 24%, indicating efficient radiative decay in the solid state. In contrast, **Th-TPA-(CN)₂** displayed a broader orange-red emission centered at approximately 605 nm, accompanied by a comparatively lower quantum yield of 18% (**Figure 4** and **Figure S17**). The emission maximum of the thiophene derivative is red-shifted by nearly 45 nm relative to its phenyl analogue, demonstrating the significant influence of the π -spacer on the electronic structure of the molecules. The observed bathochromic shift can be attributed to the stronger electron-donating nature and enhanced π -conjugation of the thiophene spacer, which facilitates more effective electronic communication between the triphenylamine donor and the dicyanostilbene acceptor. Consequently, the emission color can be systematically tuned from yellow for **Ph-TPA-(CN)₂** to orange-red for **Th-TPA-(CN)₂** substituting by the phenyl π -spacer with a thiophene unit. To further examine the stimuli-responsive luminescence of these materials, their mechanofluorochromic (MFC) behavior was investigated by comparing the solid-state emission spectra before and after mechanical grinding. Upon grinding, both **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂** exhibited a noticeable decrease in fluorescence intensity; however, no appreciable shift in the emission maximum was observed. Since mechanofluorochromic materials typically exhibit a distinct change in emission wavelength or color resulting from mechanically induced phase or molecular packing transformations, the absence of any significant spectral shift indicates that neither compound undergoes such structural changes upon grinding.

2.5 DFT studies:

Further, to gain deeper insight into the electronic structures and to correlate the experimental photophysical properties of **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂**, density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p) level of theory using the Gaussian 09 program package³⁶. The optimized frontier molecular orbital (FMO) distributions reveal that the HOMO is predominantly localized over the triphenylamine (TPA) donor with partial delocalization onto the π -spacer, whereas the LUMO is mainly concentrated on the dicyanostilbene acceptor unit (**Figure 5** and **Table S3-4** (DFT coordinates of the target compounds)). This distinct spatial separation of the frontier orbitals confirms the occurrence of an efficient intramolecular charge transfer (ICT) transition from the electron-rich TPA donor to the electron-deficient cyanostilbene acceptor upon photoexcitation.

Importantly, the nature of the π -spacer significantly influences the electronic structure of the conjugated system. Replacement of the phenyl spacer with the more electron-rich thiophene spacer enhances π -electron delocalization and facilitates stronger electronic communication between the donor and acceptor units. As a consequence, **Th-TPA-(CN)₂** exhibits a lower LUMO energy level and a smaller HOMO–LUMO energy gap than **Ph-TPA-(CN)₂**. The reduced energy gap accounts for the experimentally observed bathochromic shift in both the absorption and emission spectra of the thiophene derivative, including the appearance of a low-energy absorption shoulder around 450 nm. The DFT results are in excellent agreement with the experimental photophysical data, demonstrating that π -spacer engineering effectively modulates the frontier molecular orbital energies, the extent of ICT, and the optical band gap. These findings establish that incorporation of a thiophene π -spacer is an efficient strategy for enhancing conjugation, strengthening donor–acceptor interactions, and tuning the absorption and emission characteristics of triphenylamine–cyanostilbene fluorophores.

The electronic structures and excited-state transitions of the compounds were further examined through TD-DFT calculations, employing the B3LYP, M06, and M06-2X functionals with the 6-31G(d,p) basis set to assess their theoretical absorption characteristics. Solvent effects were incorporated using the polarizable continuum model (PCM) with dichloromethane as the implicit solvent to closely mimic the experimental conditions. A comparative assessment of the three functionals revealed significant differences in their predictive performance. Both B3LYP and M06 showed noticeable deviations from the experimental absorption spectra such as approximately 30–50 nm higher than the experimental values. In contrast, the M06-2X functional reproduced the experimental absorption maxima with significantly improved accuracy and provided more reliable vertical excitation energies and oscillator strengths, particularly for the low-energy intramolecular charge-transfer (ICT) transitions (**Figure S18-19** and **Table S5-6** (TDDFT and vertical transitions of target compounds)).

3.0 Conclusions

In conclusion, two novel unsymmetrical triphenylamine–cyanostilbene donor–acceptor fluorophores, **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂**, were successfully designed, synthesized, and structurally characterized. Systematic photophysical investigations revealed that π -spacer engineering effectively modulates the electronic structure and optical properties of these fluorophores. Compared with **Ph-TPA-(CN)₂**, **Th-TPA-(CN)₂** exhibited a ~30 nm bathochromic shift in both absorption and emission spectra owing to enhanced π -conjugation and stronger intramolecular charge transfer (ICT), which was further supported by DFT and TD-DFT calculations. Both compounds exhibited positive solvatochromism and good solid-state emission with fluorescence quantum yields of 24% for **Ph-TPA-(CN)₂** and 18% for **Th-TPA-(CN)₂**. Notably, **Ph-TPA-(CN)₂** displayed aggregation-caused quenching (ACQ), whereas **Th-TPA-(CN)₂** exhibited aggregation-induced emission enhancement (AIEE), highlighting the decisive role of the π -spacer in controlling aggregation behavior. Overall, this study demonstrates that π -spacer engineering is an effective strategy for tuning ICT, aggregation behavior, and solid-state emission in triphenylamine–

cyanostilbene fluorophores, providing useful design guidelines for developing efficient solid-state luminescent materials.

Declarations

ASSOCIATED CONTENT

Data Availability statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

^1H NMR, ^{13}C NMR, HRMS, photophysical data, DFT and TD-DFT results (PDF)

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Notes

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Author Contribution

N.S and A. N: Data Curation, Investigation, Methodology, P.R.N: Investigation, Writing-original draft, CASP: Data Curation, Formal analysis, Conceptualization, Validation, Investigation, Formal analysis, Review and editing. All authors reviewed the manuscript.

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Scheme 1

Scheme 1 is available in the supplementary files section.

Figures

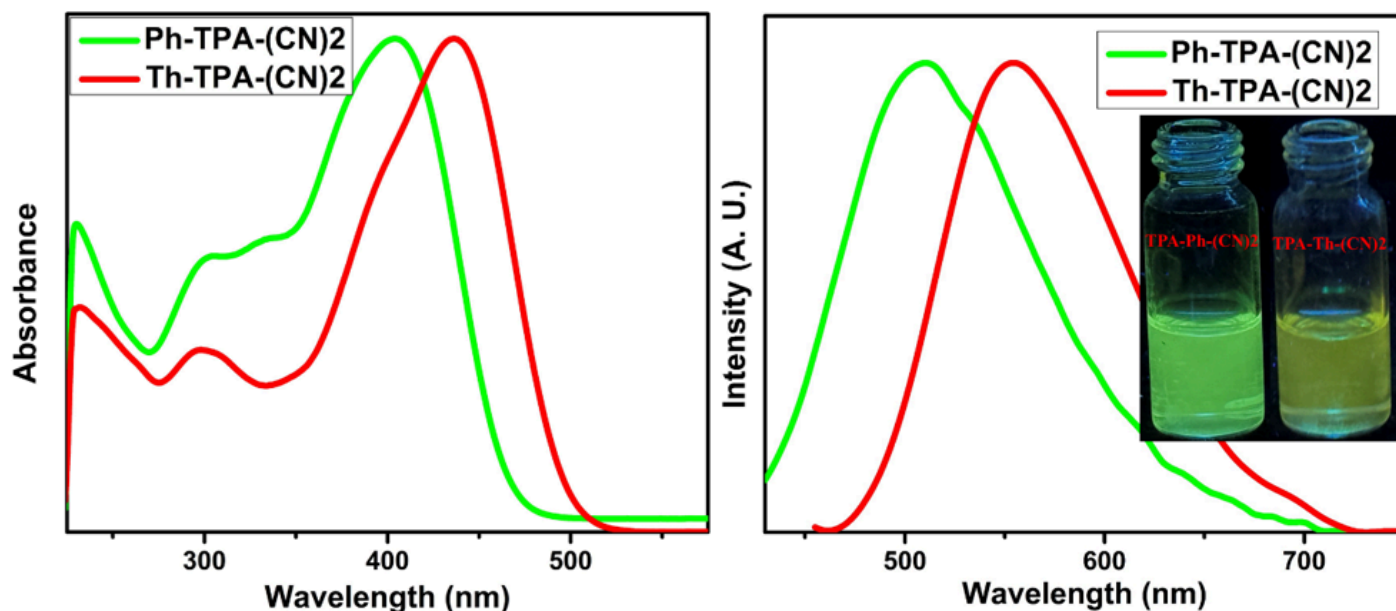


Figure 1

Absorption (left) and Emission (right) of **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂**

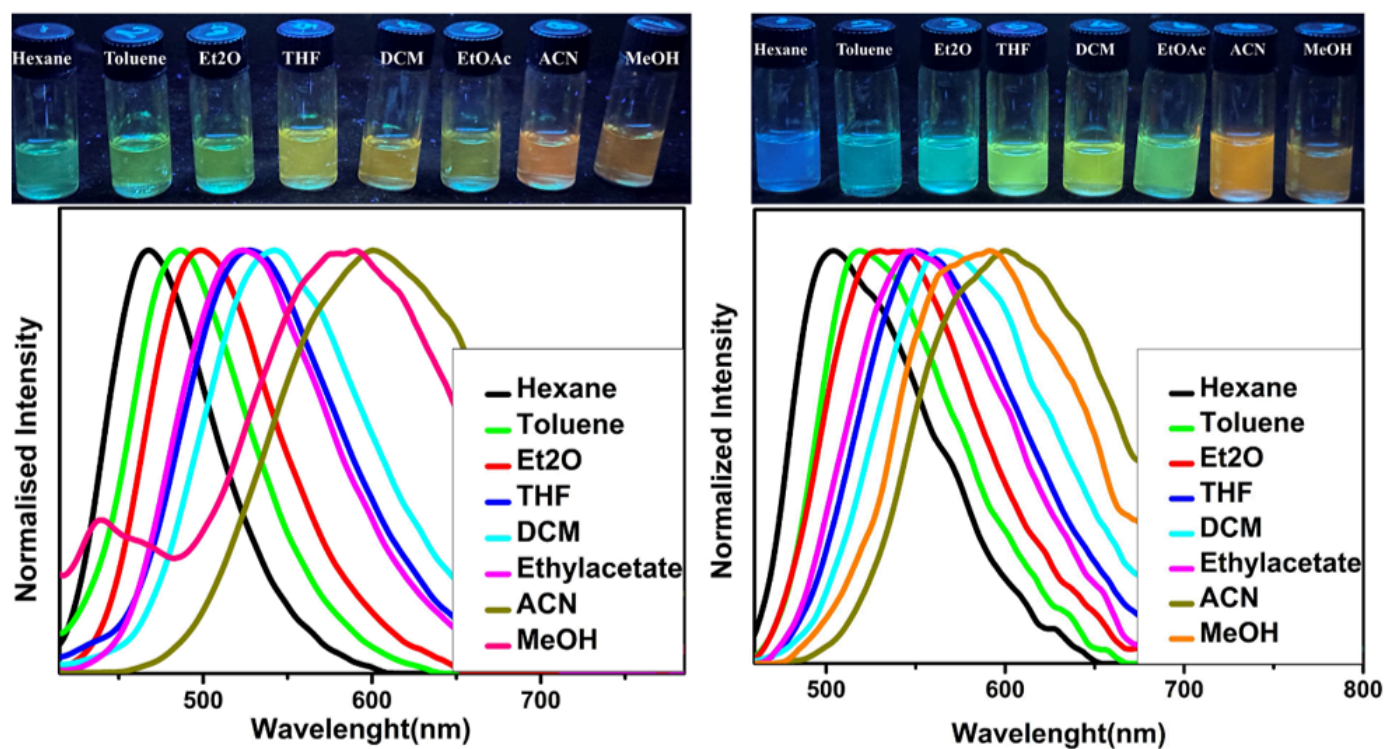


Figure 2

Emission spectra of **Ph-TPA-(CN)₂** (left) and **Th-TPA-(CN)₂** (right) in different polarity solvents. Digital photos taken under UV 365 nm are displayed on the top of the spectra.

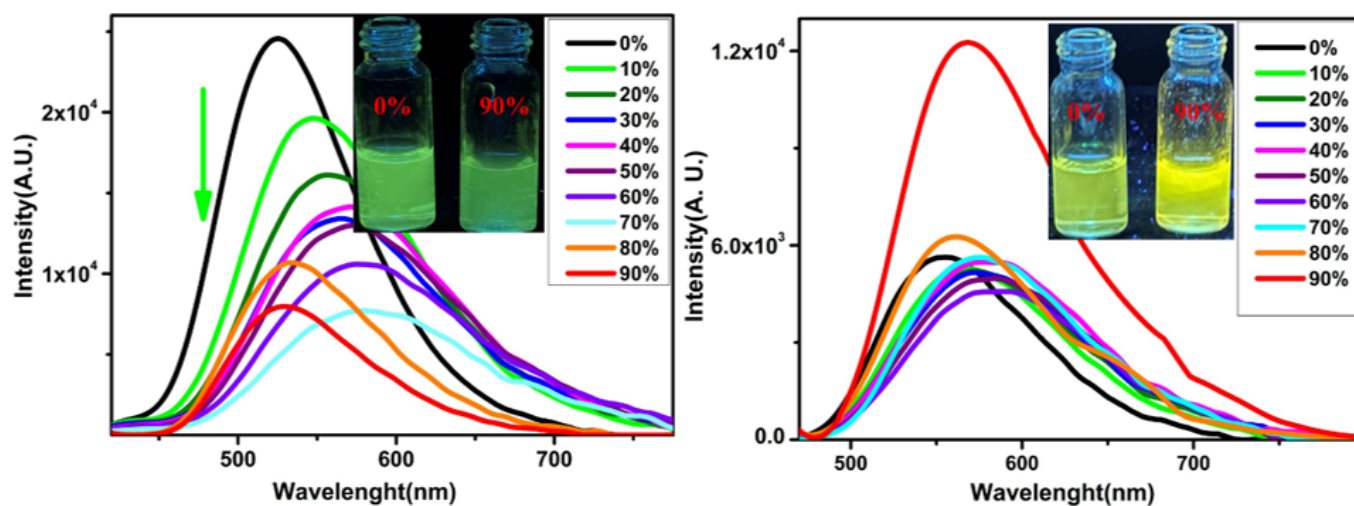


Figure 3

Aggregation studies of **Ph-TPA-(CN)₂** (left) and **Th-TPA-(CN)₂** (right)

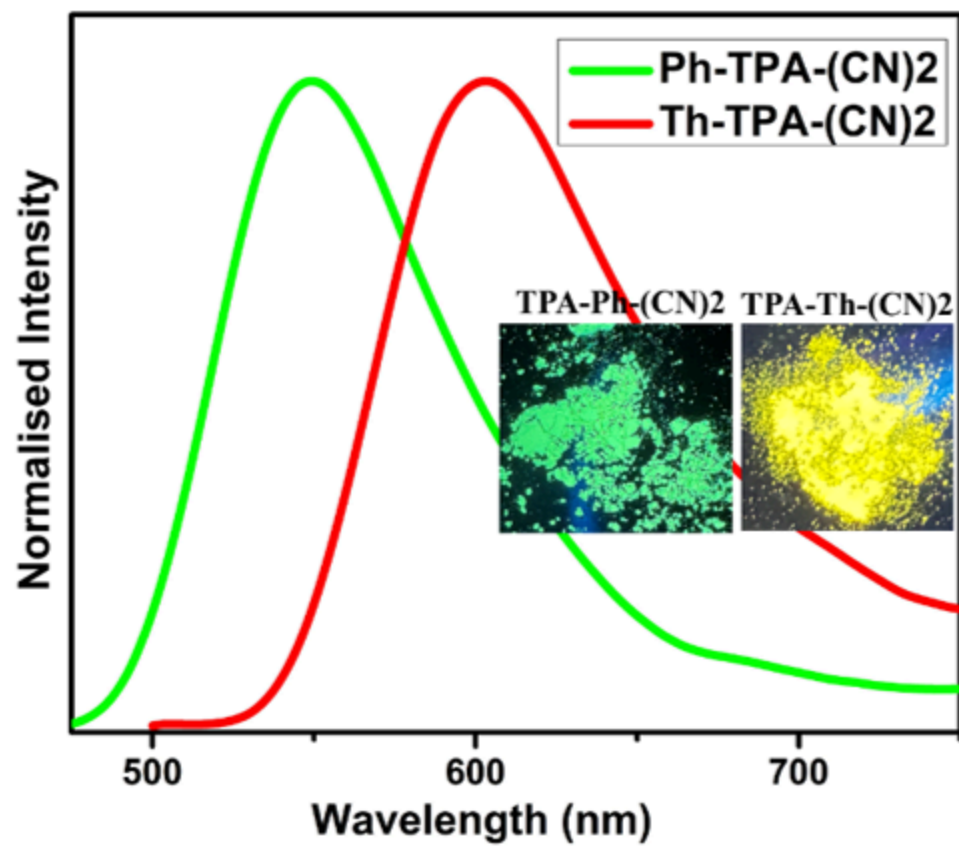


Figure 4

Solid state emission spectra of **Ph-TPA-(CN)₂** and **Th-TPA-(CN)₂**

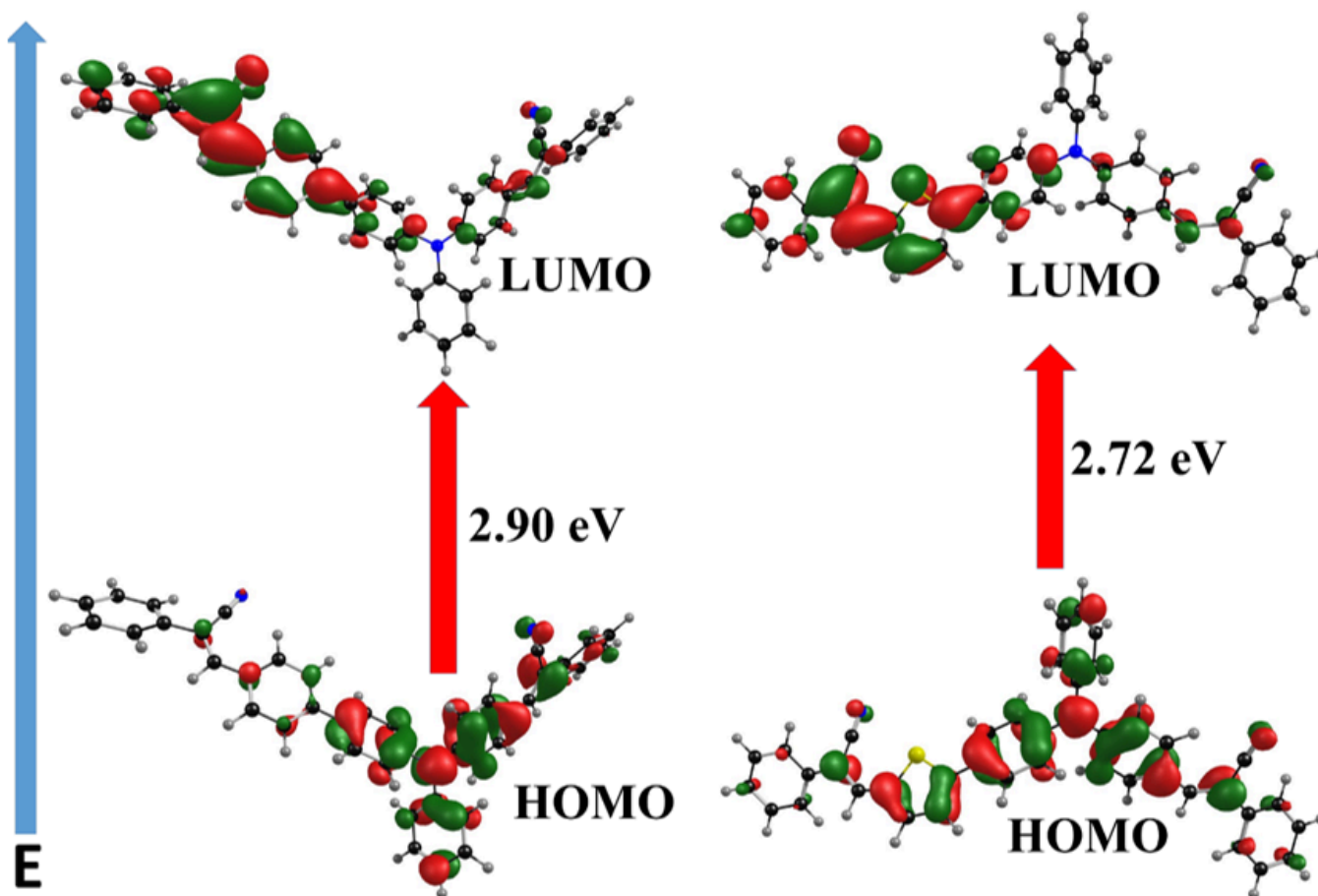


Figure 5

FMO's and calculated band gap for **Ph-TPA-(CN)₂** (left) and **Th-TPA-(CN)₂** (right)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupportingInformation.pdf](#)
- [Scheme1.png](#)