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Graphic abstract

Aggregation-induced emission of triphenylamine substituted cyanostyrene derivatives

New triphenylamine substituted cyanostyrene luminogens (G1, G1-N and G2) with aggregation-induced emission (AIE) were synthesized.
Cite this: DOI: 10.1039/c0xx00000x

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AGGREGATION-INDUCED EMISSION OF TRIPTYPHENYLAMINE SUBSTITUTED CYANOXYRENE DERIVATIVES†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Cyanostyrene-based D-π-A type conjugated compounds bearing triphenylamine units (G1, G1-N and G2) have been synthesized. By tuning the conjugated skeleton and the withdrawing electron ability of the acceptor, green, orange and red light emitters were achieved. It is interesting that although their emissions in solutions were weak, we observed strong emission in solid states. For example, the Φf of the dendritic molecule G2 in power reached 0.67, which was more than 20 times of that in THF. The single crystal X-ray diffraction data revealed that the intermolecular H-bonds of C-H···O, C-H···N and C-H···π led to the increased rigidity of the molecular skeleton, which would restrict the intramolecular rotation, yielding high Φf in solid states. These AIE compounds may become candidates for emitting materials.

Introduction

Organic π-conjugated molecules have been intensively studied due to their potential applications in opto-electronic materials.1-5 Most of organic luminogens are highly emissive in dilute solutions but exhibit weak or quenching fluorescence upon increasing the concentrations of the solutions or in the solid states because of strong π-π interactions and non-radiative decay process. This phenomenon, which is known as aggregation-caused quenching (ACQ),6,7 has greatly limited the practical applications. Numerous efforts have been made to tackle this problem,8-9 and the most important development in this field was the introduction of the term of aggregation-induced emission (AIE) by Tang and co-workers in 2001.10 They found that 1-methyl-1,2,3,4,5-pentaphenylsilole gave very weak emission in solution, but the obtained nanoparticles could emit strong fluorescence because of restriction of intramolecular rotation (RIR). Additionally, Park reported that 1-cyano-trans-1,2-bis-(4’-methylbiphenyl)-ethylene (CN-MBE) was non-luminescent in solution but highly emissive in the aggregated states.11-12

Because the achievement of the emitting materials with strong emission in solid states is important in their applications in OLEDs, laser devices, and so on, various conjugated organic molecules emitting different colors have been synthesized.13 For example, the oligofluorenes were linked to different cores, such as porphyrin and tetraphenylsilica, to give red and blue emission in OLEDs, respectively.14,15 The trimer of tetraphenylethene (TPE) gave a fluorescence peak at 494 nm, which shifted to 575 nm when fumaronitrile was used as a center linked to TPE units. In addition, an emission at 713 nm was achieved in fumaronitrile-centered TPE bearing terminal N,N-diethylamino group.16 Tian and coworkers designed a series of 2,2’-biindenyl-based fluorophores with strong solid-state emissions ranged from deep blue to red, which were tuned by the variation of the substituents on the 2,2’-biindenyl unit or by adjustment of the aggregation state.17 Moreover, the luminogens emitting blue, green, and red colors constructed from tetraphenylethene, benzo-2,1,3-thiadiazole and thiophene were prepared.18,19 It is known that triphenylamine (TPA) has been widely used as the electron donor (D) in opto-electronic materials on account of its good hole transport mobility20-22 and the cyanostyrene is a typical electron acceptor (A) group with AIE activity.23-25 Recently, Tian found that the multi-branched D-π-A-π-D compounds using triphenylamine (or carbazole) group as electron-donor, cyanostyrene (or triazine) group as electron-acceptor showed excellent two-photon absorption activity and AIE properties.26

Herein, in order to prepare new AIE materials emitting different colors we designed D-π-A conjugated compounds bearing TPA and cyanostyrene units G1, G1-N and G2 (Scheme 1). Although their emission in solutions was weak, we observed strong emission in green, orange and red in solid states, which were tuned by the conjugated length and the withdrawing electron ability of the acceptor. For example, the second generation of triphenylamine-based dendron was involved in G227-29 leading to larger conjugation than that of G1, so G2 emitted orange light and G1 emitted green light in solid states. When nitro group was introduced to cyanostyrene unit, red emitting compound G1-N was obtained.30 The single crystal X-ray diffraction data revealed that the intermolecular H-bonds of C-H···O, C-H···N and C-H···π led to the increasing rigidity of molecular skeleton, which would restrict the intramolecular rotation, yielding high Φf in solid states. Therefore, green, orange and red emitting compounds with AIE were obtained, which might have potential applications in organic light emitting materials.
Results and discussion

Syntheses

The synthetic routes for triphenylamine substituted cyanostyrene derivatives are described in Scheme 1. Firstly, the formyl-ended triphenylamine derivatives 1 and 2 were prepared according to the methods reported by our group previously.\textsuperscript{31} The Knoevenagel condensation reaction between formyl-ended triphenylamine derivative (compound 1 or 2) and phenylacetonitrile catalyzed by sodium hydroxide afforded G1\textsuperscript{32} and G2 in yield of 85% and 79%, respectively. Similarly, the Knoevenagel condensation reaction between compound 1 and 2-(4-nitrophenyl)acetonitrile catalyzed by tetrabutylammonium hydroxide (TBAH) gave G1-N in a yield of 90%. All the new compounds were characterized with FT-IR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and MALDI/TOF mass spectroscopy, and they are soluble in dichloromethane, chloroform and THF. From the FT-IR spectra for G2 we found the vibration absorption band appeared at ca. 960 cm\textsuperscript{-1}, meaning that the carbon-carbon double bonds adopted in trans-forms. In addition, the \textsuperscript{1}H NMR spectra of G2 further confirmed that ethenyl groups adopted the trans-conformation on account of the absence of the signal at ca. 6.5 ppm assigned to the protons in cis-double bonds.\textsuperscript{31}

UV-vis absorption and fluorescence emission spectra

The UV-vis absorption and fluorescence emission spectra of triphenylamine substituted cyanostyrene derivatives G1, G1-N and G2 in THF (1.0×10\textsuperscript{-5} M) were shown in Figure 1a and the

\begin{figure}[h]
\centering
\includegraphics{figure1}
\caption{Fig. 1 a) UV-vis absorption and fluorescence emission (\(\lambda_{\text{ex}} = 365\) nm) spectra of G1, G1-N and G2 in THF (1.0×10\textsuperscript{-5} M); b) Fluorescence emission spectra of G1, G1-N and G2 in solid states (\(\lambda_{\text{ex}} = 365\) nm).}
\end{figure}
Table 1: UV-vis absorption and fluorescence data of triphenylamine derivatives.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Solution</th>
<th>Powder</th>
<th>Crystal</th>
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<tr>
<td></td>
<td>$\lambda_{ab}/$nm</td>
<td>$\lambda_{em}$/nm</td>
<td>$\Phi_e$</td>
</tr>
<tr>
<td>G1</td>
<td>298, 398</td>
<td>494</td>
<td>0.02</td>
</tr>
<tr>
<td>G1-N</td>
<td>439</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>G2</td>
<td>303, 406</td>
<td>584</td>
<td>0.03</td>
</tr>
</tbody>
</table>

* Excited at 365 nm.

Quantum yields ($\Phi_e$) determined in THF using an integrating sphere.

Quantum yields ($\Phi_e$) determined using an integrating sphere.

Not obtained.

Fig. 2: Photos of G1, G1-N and G2 in THF (a, b and c, respectively) and in powders (d, e and f, respectively) under UV illumination (365 nm), and fluorescent microscopy ($\lambda_{em}=330-385$ nm) images of G1 (g) and G1-N (h) in crystals.

The corresponding photophysical data are presented in Table 1. Two clear absorption peaks at ca. 300 nm and 400 nm were detected for compounds G1 and G2. The former one can be attributed to the $\pi-\pi^*$ transition of triphenylamine group and the latter one can be assigned to the intramolecular charge transfer (ICT) band. In detail, the absorption bands of G1 were located at 298 nm and 398 nm, which red-shifted to 303 nm and 406 nm for G2 due to the enlarged conjugation of the increased dendritic structure. On account of the introduction of nitro group the maximum absorption of G1-N red-shifted to 439 nm, and its absorption intensity was quite lower than that of G1 due to the spin-forbidden charge transfer.\(^3\) It is notable that the intensities of the absorption peaks for G2 was higher than G1 and G1-N due to the increased number of vinyl triphenylamine units in G2. From the fluorescence emission spectra of G1, G1-N and G2 in THF we can find that G1-N was almost non-emissive because the introduction of electron withdrawing group of nitro into cyanostyrene unit might lead to the occurrence of photo-induced electron transfer from triphenylamine to the accepter. G1 gave a weak emission at 494 nm. With increasing the generation of the dendron based on triphenylamine, a red-shift of emission band located at 584 nm was observed for G2 due to the larger $\pi$-conjugation. The fluorescent quantum yields ($\Phi_e$) of G1, G1-N and G2 in THF were 0.02, 0.01 and 0.03 using an integrating sphere, meaning that the emission was very weak.

The fluorescence emission spectra of G1, G1-N and G2 in powders or in crystals were shown in Figure 1b. It was found that the emission of G1 and G2 in powders appeared at 506 nm and 596 nm, respectively, with a red-shift compared with those in solutions due to the aggregation. Although G1-N was non-emissive in solution, its powder gave an obvious emission at 652 nm. Notably, the $\Phi_e$ values for these compounds in powders were more than 20 times of those in solutions (Table 1), indicating they exhibited AIE properties. Moreover, the crystals of G1 and G1-N (the crystal of G2 was not obtained) also gave strong emission, and their emission bands further red-shifted to 516 nm and 658 nm in the crystals. The $\Phi_e$ values for G1 and G1-N in crystals were 0.31 and 0.06, respectively, which were similar to those in powders. In addition, the photos of G1, G1-N and G2 in solutions and in solid states illuminated by UV light as shown in Figure 2 further illustrated that the emission was enhanced significantly in powders as well as in crystals compared with that in solutions.

Electrochemical properties

The electrochemical behaviors of triphenylamine substituted cyanostyrene derivatives were investigated by cyclic voltammetry (CV) using a standard three-electrode cell and an electrochemical workstation (CHI 604) under N\(_2\) atmosphere. Figure 3 showed the cyclic voltammogram (CV) diagrams of G1, G1-N and G2 using 0.1 M tetrabutylammonium tetrafluoroborate (TBABF\(_4\)) as supporting electrolyte in dry CH\(_2\)Cl\(_2\), with a glass carbon disc working electrode, a platinum-wire counter electrode, and an SCE reference electrode. The SCE reference electrode was calibrated using the ferrocene/ferrocenium (Fc/Fc\(^+\)) redox couple as an external standard. According to the redox potential of Fc/Fc\(^+\) (with an absolute energy level of ~4.8 eV relative to the vacuum level for calibration), the HOMO energy level was calculated to be -5.52 eV for G1, -5.52 eV for G1-N and -4.91 eV for G2 (Table S1), respectively. The higher HOMO energy level of G2 indicated its strong electron donating ability. The calculated LUMO energy level for G1-N (-3.10 eV) was lower than that of G1 (-2.78 eV) and G1 (-2.35 eV) due to the strong accepting ability of the nitro group.
**AIE properties**

As discussed above, compounds G1, G1-N and G2 exhibited AIE behaviors. In order to evaluate the AIE properties of these compounds, G2 was selected as an example. The UV-vis absorption and fluorescence emission spectral changes of G2 in the THF/water (G2 is soluble in THF and water is a poor solvent) with different amount of water were given in Figure 4. It was found that when the amount of water was ≤ 50 % (volume content) the UV-vis absorption spectra of G2 were similar to that in pure THF. Upon further increasing of the amount of water, the absorption band at 406 nm red-shifted and was broadened, which might be due be the molecular aggregation. For example, the absorption red-shifted to 420 nm and 422 nm when the contents of water were 70 % and 90 % in THF/water, respectively. In addition, the appearance of tails in the visible region could be attributed to Mie scattering caused by nanoparticles. From Figure 4b, we could find that the emission of G2 can hardly be detected when the volume content of water was ≤ 50% in THF/water. However, with further increasing the amount of water in the system, the fluorescence emission of G2 was enhanced significantly, accompanied with a blue-shift. The emission appeared at 582 nm and 573 nm when the volume contents of water were 70 % and 90 % in THF/water, respectively. In addition, we presented the plot of the ratio of I/I₀, in which I was the integral of fluorescence emission in the mixed solvent and I₀ was that in pure THF, vs the content of water in THF/water. As shown in inset of Figure 4b, when the volume content of water was ≤ 50%, I/I₀ values were quite low. With increasing the content of water, I/I₀ values increased significantly, suggesting AIE happened in the aggregates of G2.

**X-ray studies of the single crystals**

In order to reveal the mechanism of the AIE phenomena, we tried to get single crystals for all compounds. The crystals of G1 and G1-N were obtained from the solutions in petroleum ether/chloroform, but we could not get the crystal of G2. The single crystal study revealed that the crystal structures of G1 and G1-N belonged to the monoclinic space group P2(1)/n and monoclinic space group P2₁/c, respectively, and each cell contained four molecules (Z = 4). The molecular ORTEP drawings were displayed in Figure 5. In the crystal of G1, the torsion angle between phenyl rings P3 and P4 was 56.78(21)°, exhibiting more twisting structure of cyanostyrene than that in G1-N (8.38(6)°). The twisting structures between two phenyl rings in G1 reduce the conjugation of molecules and prevent face-to-face π-π aggregations. Moreover, the intermolecular interactions among molecules G1 were shown in Figure 6a. It was found that the H-bond (2.44 Å) between N (in C-N triple bond) and vinyl-H atom in two adjacent molecules was formed along the short axis of the molecule. The C24-H····π (P₃) (2.87 Å) and C4-H····π (P₃) (2.93 Å) provided two kinds of interactions for each P₃ ring. These C-H····N and C-H····π interactions resulted in a rigid three-dimensional network. Thus, the twisting structure (torsion angle between P3 and P4) and the existence of multiple C–H····π H-bonds restricted the intramolecular rotation and...
enabled the molecule to emit light intensively in the solid states.\(^{34}\)

In the crystal of \textit{G1-N} (Figure 6b-c), the rings of P3 and P4 were almost coplanar (torsion angle 8.38(6)°) and four kinds of H-bonds were formed. C18-H···N2 (2.58Å) and C24-H···O1 (2.62 Å) linked the molecules in each layer together along the P3 and P4 plane. Each H-bond of C2-H···O1 (2.60 Å) connected one pair of molecules in adjacent layers, and the H-bond of C5-H···O2 (2.65 Å) provided a head-to-tail type connection. Meanwhile, the C-H···π interactions of 2.61 and 2.93 Å happened between parallel non-planar molecules. Accordingly, RIR process caused by the intermolecular interactions, including C-H···π, C-H···N and C-H···O, resulted in the increased rigidity of molecular skeleton to yield higher \(\Phi_F\) in crystals than those in solutions.

**Fig. 6** Intermolecular H-bonds (C-H···O, C-H···N and C-H···π) in the crystals of \textit{G1} (a) and \textit{G1-N} (b, c).

**Conclusions**

In conclusion, cyanostyrene-based D-π-A conjugated compounds bearing triphenylamine units (\textit{G1}, \textit{G1-N} and \textit{G2}) have been synthesized. By tuning the conjugated skeleton and the withdrawing electron ability of the acceptor, green, orange and red light emitters were achieved. It is interesting that although their emissions in solutions were weak, we observed strong emissions in solid states. For example, the \(\Phi_F\) of dendritic molecule \textit{G2} in power reached 0.67, which was more than 20 times of that in THF. The single crystal X-ray diffraction data revealed that the intermolecular H-bonds of C-H···O, C-H···N and C-H···π led to the increased rigidity of the molecular skeleton, which would restrict the intramolecular rotation, yielding high \(\Phi_F\) in solid states. Therefore, the green, orange and red emitting compounds with AIE properties were obtained, which might have potential applications in organic light emitting materials.

**Experimental Section**

**General**

Solvents were purified and dried using standard protocols. All other chemical reagents were obtained commercially and were used as received without further purification. \(^1\)H NMR spectra were recorded on a mercury plus 400 MHz using CDCl\(_3\) as solvent in all cases. \(^{13}\)C NMR spectra were recorded on a mercury plus 100 MHz using CDCl\(_3\) as solvent. FT-IR spectra were measured using a Germany Bruker Vertex 80v FT-IR spectrometer by incorporating samples in KBr disks. Mass spectra were performed on Agilent 1100 MS series and AXIMA CFR MALDI/TOF (Matrix assisted laser desorption ionization/Time-of-flight) MS (COMPACT). UV-vis absorption spectra were determined on a Shimadzu UV-1601PC spectrophotometer. Fluorescence emission spectra were carried out on a Shimadzu RF-5301 luminescence spectrometer. The emission spectra of solids were recorded using Maya2000 Pro CCD spectrometer. The absolute fluorescence quantum yields were measured on Edinburgh FLS920 steady state fluorimeter. The fluorescence microscopy images were obtained from Olympus BX51 fluorescence microscope. Cyclic voltammetry was carried out with a CHI 604B electrochemical working station at room temperature at a scan rate of 50 mV/s.

**Synthetic procedures and characterizations**

\textit{(Z)-3-(4-(diphenylamino)phenyl)-2-phenylacrylonitrile} (G1)

A mixture of formyl-ended triphenylamine derivative 1 (0.6 mmol), phenylacetonitrile (0.9 mmol), and sodium hydroxide (0.9 mmol) in ethanol (50 mL) was stirred for 24 h at room temperature under an atmosphere of nitrogen. Then, the precipitate was filtered off, washed with cold ethanol. Yield: 85%. M.p. 148.0-151.0 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.774 (d, \(J = 8\) Hz, 2H), 7.642 (d, \(J = 8\) Hz, 2H), 7.402-7.440 (m, 3H), 7.294-7.324 (m, 3H), 7.324-7.361 (m, 5H), 7.100-7.168 (m, 6H), 7.048 (d, \(J = 8\) Hz, 2H) \((\text{Figure S1})\). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.98, 146.66, 141.73, 135.08, 130.69, 129.02, 128.60, 126.50, 125.73, 124.41, 120.96, 118.79, 107.80 \((\text{Figure S2})\). FT-IR (KBr, cm\(^{-1}\)):

2216, 1583, 1506, 1489, 1448, 1329, 1298, 1192, 1178, 831, 760, 696. MS, m/z: cal: 372.16, found: 372.9 \((\text{Figure S3})\).
Preparation of aggregates for AIE measurement

The solution of G2 in THF was firstly prepared (1.0×10⁻⁵ M). Then, 1 mL of the above solution was transferred to a volumetric flask (10 mL). After adding an appropriate amount of THF, water was added dropwise under vigorous stirring to furnish a 10 mL solution in a THF/water with a specific water fraction. The water content was varied in the range of 0-90 vol %. The UV-vis absorption and fluorescence emission spectra of the resulting samples were measured immediately after preparation.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (51073068, 21374041), the 973 Program (2009CB939701), and the Open Project of the State Key Laboratory of Supramolecular Structure and Materials (SKLSSM201203).

Notes and references

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2 Key Laboratory of Functional Inorganic Material Chemistry (MOE), School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, PR China.
† Electronic Supplementary Information (ESI) available: Electrochemical properties, 1H-, 13C-NMR spectra and MALDI/TOF MS spectra. See DOI: 10.1039/b000000x/

Table 2 Crystal data for G1 and G1-N.

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<th>Compound</th>
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<th>G2</th>
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<td>C₂₇H₃₈N₂</td>
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<tr>
<td>Formula wt</td>
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</tr>
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<td>11.154(2)</td>
</tr>
<tr>
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<td>7.5463(15)</td>
</tr>
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<td>c, Å</td>
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<td>wR₂ (all data)</td>
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B. Li, Q. Li, B. Liu, Y. Yue and M. Yu, Dyes Pigments, 2011, 88, 301.

