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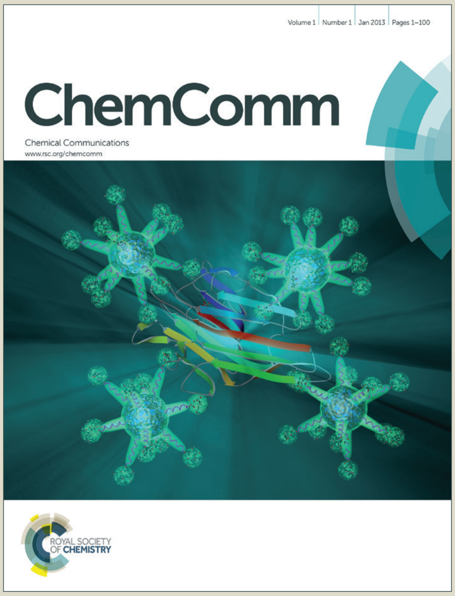

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ARTICLE TYPE

Charge Instability of Symmetry Broken Dipolar States in Quadrupolar and Octupolar Triphenylamine Derivatives

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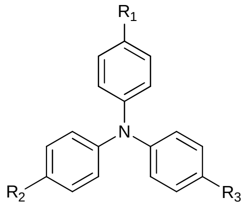
The quadrupolar and octupolar cyano triphenylamines shows symmetry broken dipolar charge transfer state, however its stability can be controlled by the rotation of N-C bond of amino and phenylene moiety.

• Photoinduced intramolecular charge-transfer (ICT) interactions, one of the primary photochemical processes has been of great interest as the magnitude of ICT has a significant influence on the functions and efficiencies of molecular systems in the fields of photovoltaics,[1] non-linear optics,[2] fluorescent sensors,[3] and organic light emitting diodes (OLED).[4] Recently, it has been found that molecule having multiple donors (D) or acceptors (A) such as D-D-π-A[5], D-π-A-A,[6] $D-(\pi-A)_2$ or $A(\pi-D)_2$ (quadrupolar), and $A(\pi-D)_3$ or $D(\pi-A)_3$ (octupolar)[7] motif show higher efficiency in solar cells, multi-photon absorbing property when compared to the single-arm parent compound with D-π-A motif. The intramolecular charge transfer interactions and subsequent charge redistribution upon excitation has been identified as one of the important factor responsible for the enhanced properties of multipolar chromophores. Most of the work reported so far was focussed on the structure-property relationship with respect to the dipolar, quadrupolar, and octupolar nature to the nonlinear optical properties. No systematic photophysical studies to understand the nature and stability of the CT states, magnitude of CT interactions has been reported so far to the best of our knowledge.

While the CT interaction of simple D-π-A motif can be explained by the solvatochromism in fluorescence accompanied by large changes in dipole moments that of multipolar systems might either be originated from the cumulative behaviour of whole molecule with zero dipole moment change or symmetry broken dipolar ICT state from the subchoromophoric, single arm groups.[8] Thus formed states may not have the same stability because the donor/acceptor groups which are not part of the CT state would destabilize by competing to become part of the CT state. Further, most of the molecules studied so far are based on the vibronic coupling between the branches and no system based on the rotational motion of the bond has been reported. Hence, we have chosen the triphenylamine derivatives shown in Chart 1 with one (**mCN**), two (**dCN**), and three (**tCN**) cyanide groups substituted at the para positions, which are respectively having the dipolar, quadrupolar, and octupolar configurations to understand the CT interactions.

Chart 1



	R_1	R_2	R_3
mCN	CN	H	H
dCN	CN	CN	H
tCN	CN	CN	CN

The cyano substituted triphenylamines, 4-(diphenylamino) benzonitrile (**mCN**), 4,4'-(phenylazanediyl)dibenzonitrile (**dCN**), and 4,4',4''-nitrilotribenzonitrile (**t**CN) were synthesized and characterized using IR, ^{1}H, ^{13}C- NMR (See ESI, Figure S1-S8) and single crystal X-ray diffraction methods. The single crystal X-ray structure of **mCN** and **tCN** depicted in Figure 1 shows propeller shaped structure with no significant structural differences with respect to number of cyano groups (ESI, Table S1). The absorption and fluorescence spectra of **mCN, dCN**, and **tCN** dissolved in toluene solvent are given in Figure 2. While two absorption peaks were observed for **mCN** (302 (s), 331 nm) and **dCN** 313(s), 334 nm) that of **tCN** shows intense, single absorption peak at 336 nm, having the molar absorptivity at least two times higher than that of **mCN** and **dCN**. This feature is ascribed to the degeneracy of the S_1 state of **tCN** and also to the increased number of cyano groups that alters the electronic energy levels of TPA core through π–conjugation. Further insight about the absorption spectrum has been gained from density functional theory calculations using Gaussian 09 programme.[9a] The lowest energy electronic transition for all the TPA

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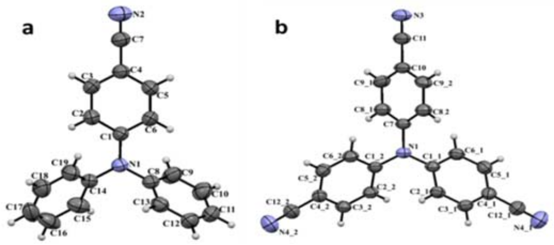


Fig.1 X-ray crystal structure of a) **mCN** and b) **tCN**

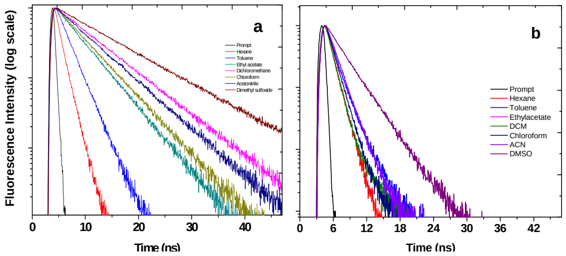


Fig.3 Fluorescence decay profiles of a) **mCN** and b) **dCN** in different solvents monitored at their respective emission maximum wavelength

derivatives are found to be originated from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (ESI, Figure S9-S11, Table S2-3). Furthermore, electron density redistribution occurs to a significant extent during electronic transition from HOMO to LUMO, which suggests the possibility of ICT interactions. To confirm, we have calculated natural transition orbitals (NTOs) of first excited state[9b] where a pronounced electron density shifts can be found between the phenylene moieties, which ascertains the CT nature of the first excited singlet state (ESI, Table S4). The fluorescence spectrum of **mCN**, **dCN**, and **tCN** in toluene has respectively been observed at 405, 387, and 369 nm. Interestingly, the mono cyanide substituted TPA show red shifted fluorescence than the di- and tri-cyanide, despites additional π–conjugation between the cyano and phenylene moieties. Notably, the backbone of **mCN** closely resembles N, N-dimethylaminobenzonitrile (DMABN), a classical example for ICT molecules whose well-studied dual fluorescence behaviours are still highly debated.[10] Nonetheless, the differences between TPA and DMABN could be; the lone pair of central nitrogen atom in TPA is delocalized through conjugation with phenylene moieties, at the expense of ICT interactions,[11] in DMABN the N-methyl groups facilitate the CT interaction by an inductive electron-donating effect with phenylene moiety. The Stokes shift values for **mCN**, **dCN**, and **tCN** was calculated to be 4040, 3230, and 2750 cm^{-1}. Being with the same molecular skeleton, the larger difference in the Stokes shift values reflects that the magnitude of charge transfer from TPA, donor to cyanide acceptor decreases when more than one cyanide group is present. While the simple donor-acceptor systems forms dipolar, D^{+}A^{-} charge separated state, quadrupolar and octupolar system show respectively either symmetric, non-solvatochromic, quadrupolar ($A^{\delta-}D^{+}A^{\delta-}$) and octupolar ($A^{\delta-}D^{+}(A^{\delta-})A^{\delta-}$) CT state or symmetry broken, solvatochromic, dipolar CT state.[12] As can be seen from Figure 2, **dCN** and **tCN** also show solvatochromism in fluorescence similar to **mCN**. The observed fluorescence might have been originated from the symmetry broken dipolar CT state which is localized on one of the donor-acceptor pair (Scheme 1). A quantitative measure for CT efficiency, the slope of the Lippert-Mataga plot[13] was calculated to be 15400, 5300, and 9600 cm^{-1} respectively for **mCN**, **dCN**, and **tCN** (ESI, Figure S12). Interestingly, the excited state dipole moments (ESI, Table S5) was calculated to be 8.1, 15.0, 11.0 D respectively for **mCN**, **dCN**, and **tCN**. However, the difference between the ground and excited state dipole moments follows the order **mCN**>t**CN**>**dCN**, which suggests that the all the derivatives show symmetry broken intramolecular charge transfer interactions which are in fact strongly influenced by number of donor-acceptor pairs.

The fluorescence decay profiles measured using time correlated single-photon counting (TSCPC) technique by exciting the sample at 350 nm, ~200 ps pulsed light are given in Figure 3 and Figure S13 (ESI, Table S6). For all TPA derivatives, longer lifetimes were observed in polar solvents. Specifically, the fluorescence lifetime of **mCN** has increased at least by ~20 times while going from nonpolar, hexane (0.6 ns) to polar, DMSO (10 ns). This feature suggests that the polar CT state might have been stabilized by the polar solvents. The radiative and non-radiative rate constants calculated from the fluorescence quantum yields and lifetime suggests that the radiative rate constant (K_r) becomes enhanced by a factor of 8, 4, and 5 times respectively for **mCN**, **dCN** and **tCN** in DMSO when compared to toluene (ESI, Table S6). On the other hand the nonradiative rate constant (K_{nr}) remains almost constant irrespective of the solvent. Thus, based on the above facts we can conclude that though **dCN** and **tCN** form symmetry broken dipolar CT state, its lifetime is shorter than that of **mCN**. Symmetry broken CT state for quadrupolar and octupolar systems can be explained respectively by two and three, isoenergetic charge resonance structures. The inter-conversion between the CT states is driven by the phenyl ring rotation around N-C bond of amine and phenyl group. Effect of phenylene rotation on the fluorescence behaviour was probed by increasing the viscosity of the solution using polystyrene, where higher viscosity is expected to hinder the N-C bond rotation. It was found, as shown in Figure 4 that the fluorescence intensity decreased with increased percentage of polystyrene (ESI, Figure S14). Indeed, up to two fold decreased fluorescence was noted for

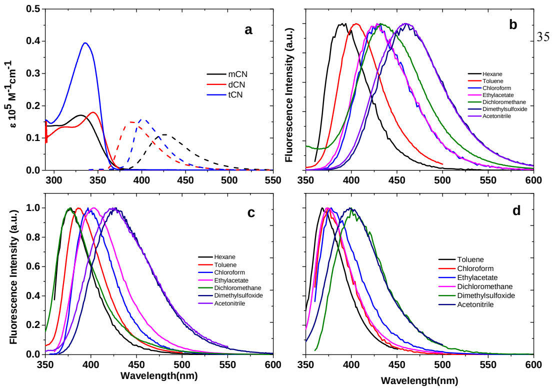
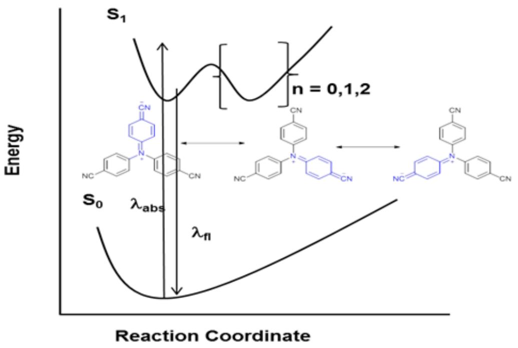


Fig.2 a) UV-visible absorption (solid line) and fluorescence spectra (dotted line) of cyanotriphenylamine derivatives in toluene. Fluorescence spectra of b) **mCN**, c) **dCN**, and d) **tCN** in different solvents.



Scheme 1 Potential energy diagram of charge resonance structures for octupolar molecule

mCN, however that of **dCN** and **tCN** was measured to be ~1.4 fold when compared to neat toluene. This observed feature underscores the importance of phenyl rotation in the CT state formation.

The schematic electronic energy level diagram of cyanotriphenylamine (**tCN**) is given in Scheme 1. According to Prof. Painelli's phase diagram for quadrupolar and octupolar molecules,[14] the cyanotriphenylamines belongs to the class I, where the nondipolar ground state undergoes symmetry breaking at the excited state having two, three equivalent minima respectively for quadrupolar and octupolar chromophores with equal and opposite dipole moments. The initial photo-excitation of the TPA derivatives populates the higher excited state which is then relaxed to form a long-lived CT state. The CT state formation involves the rotation of the phenyl ring with the subsequent formation of quinonoid type structure involving anyone of the cyanophenylene group, and then it is relaxed to the S_0 state through radiative decay. In this case, the lifetime of the CT state is controlled by the rate at which the phenyl group rotates (tunnelling); higher the rotations lower the CT state stability and vice versa. For instance, **dCN** and **tCN** show nearly two times longer fluorescence lifetime in acetonitrile and DMSO when compared to nonpolar solvent, toluene and ethyl acetate. This feature is ascribed to the stabilization of the CT state, which subsequently prevents the destabilization process by hindering the inter-conversion between the charge resonance structures by means of phenylene rotation. In order to confirm this hypothesis we have obtained the optimized geometry of the first excited state were one of the N–C bond has more double bond character for **dCN** and **tCN** when compared to the ground state (SI, Table S7-8). Thus, based on the above facts we can conclude that though the quadrupolar and octupolar molecules form the symmetry broken CT state, the lifetime of the thus formed state is significantly influenced by the remaining acceptor moieties that are not part of the CT state.

In summary, the quadrupolar and octupolar molecules with triphenylamine as donor and cyano group as an acceptor forms an emissive, long-lived, symmetry broken intramolecular charge transfer state similar to the dipolar molecule. The radiative rate constant of the CT state becomes highly sensitive to the number of donor-acceptor pair. The formation of the charge transfer state can be manipulated by the controlling the rotational motion of the phenylene moiety.

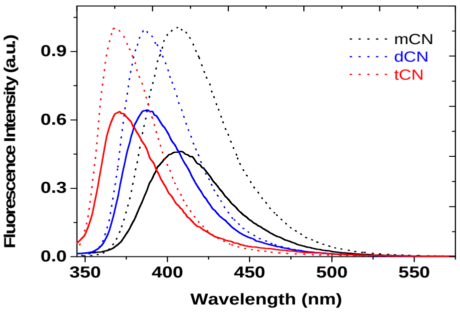


Fig. 4 Fluorescence spectra of cyanotriphenylamines in toluene (dotted lines) and in toluene with 9.5% polystyrene (solid lines)

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