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T and V-shaped donor-acceptor-donor molecules involving pyridoquinoxaline: large Stokes shift, environment-sensitive tunable emission and temperature-induced fluorochromism

Bahadur Sk, Saurabh Khodia and Abhijit Patra*

The intramolecular charge transfer-driven emission properties of T and V-shaped donor-acceptor-donor molecules involving new acceptor core of pyridoquinoxaline were demonstrated. The Tshaped molecule exhibits large Stokes shift, red emission in the solid state and remarkable viscosity and temperature-dependent tunable fluorescence including thermally-induced a singlecomponent near white-light emission.

The organic molecules with the electron donor (D) and electron acceptor (A) units connected through π -linkers emerged as important building blocks of optoelectronic materials and devices.¹ The most fundamental phenomenon governing the interesting optical properties of these molecules is an intramolecular charge transfer (ICT) from the donor to the acceptor in the excited state.² The molecular geometry has a profound impact on the ICT process.^{2a,3} Often, ICT proceeds with drastic conformational changes in certain D-A molecules leading to the formation of the twisted intramolecular charge transfer (TICT) state.^{2a,4} As the TICT emission is highly environment-sensitive and depends on the solvent polarity, viscosity and temperature of the medium, such fluorophores are potential candidates for designing optical sensors.⁵

The intramolecular relaxation process from the locally excited (LE) state to the ICT state leads to a large Stokes shift.³ The inner-filter effect due to the reabsorption of the emitted photons is avoided in fluorophores exhibiting large Stokes shift and are suitable for the cellular and sub-cellular imaging.⁶ Also, the population distribution in LE and ICT states often give rise to tunable fluorescence including white-light emission beneficial for display devices.⁷ Besides, fluorescent probes apt for the measurement of microscopic viscosity and temperature with high spatiotemporal resolutions are important for understanding the mechanisms of many biological processes.⁸



Scheme 1 The synthetic scheme of T and V-shaped donor-acceptor-donor (D-A-D) molecules PQCz-T and PQCZ-V, respectively employing carbazole (Cz) as the donor and pyridoquinoxaline (PQ) as the acceptor.

Notably, the molecular thermometer based on the ratiometric fluorescence signalling is of increasing interest.⁹ However, the coexistence of diverse properties in a single molecular platform, though highly desirable, is rare.

A modular approach is required for the cost-effective fabrication of multifunctional molecular optical materials.¹⁰ The judicious choice of the diverse building blocks and their successful integration along with the subtle variation of the molecular geometries allow the fine-tuning of photophysical properties. Herein, we designed a new class of donor–acceptor-donor (D–A–D) type molecules having a novel acceptor core of pyridoquinoxaline (PQ). The linking of electron donating carbazole at 2,7 and 3,6-positions of phenanthrene analog of PQ led to T and V-shaped molecules (PQCz-T and PQCz-V) which showed remarkable environment-sensitive photophysical properties (Scheme 1). The temperature-induced tunable emission from blue to orange including a single-component white-light emission observed in PQCz-T is unique in the context of a single molecular material.

The two sp² hybridized nitrogen atoms in quinoxaline (Qx) make it electron-deficient.¹¹ Replacing the phenyl ring in Qx by

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhauri, Bhopal 462066, Madhya Pradesh, India E-mail: abhijit@iiserb.ac.in

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Fig. 1 (a) Normalized absorption and emission ($\lambda_{ex} = 340 \text{ nm}$) spectra of PQCz-T (solid line) and PQCz-V (dotted line) in toluene (absorption: black, emission: green, i-iv) and DCM (absorption: blue, emission: red, v-viii). (b) The digital photographs of PQCz-T (upper panel) and PQCz-V (bottom panel) in solvents of varying polarity under the illumination of UV lamp ($\lambda_{ex} = 365 \text{ nm}$). A: toluene (0.099), B: 1,4-dioxane (0.164), C: tetrahydrofuran (0.207), D: chloroform (0.259) and E: dichloromethane (0.309). The solvent polarity parameter (E_T^N value) is mentioned in the parenthesis.

pyridine leads to pyridoquinoxaline (PQ) with further enhancement of electron withdrawing capability. The fused aromatic structures can be developed through oxidative coupling reactions involving PQ unit. Accordingly, we introduce PQ as a new electron-acceptor core for the construction of donor-acceptor-donor (D-A-D) triads. Considering the excellent electronic properties, high thermal stability and low-cost,12 carbazole was chosen as the electron donating unit. The bromination of phenanthraquinone at 2, 7 and 3, 6 positions followed by Schiff base condensation with 3,4-diaminopyridine yielded two variants of substituted pyridoquinoxaline respectively, PQ1 and PQ2 (Scheme 1). The Pd(II)-catalyzed Buchwald-Hartwig cross coupling reactions of PQ1 and PQ2 with carbazole led to the fabrication of compounds PQCz-T and PQCz-V having T and V-shaped molecular geometries, respectively (Schemes 1, S1, S2). The compounds were characterized by FTIR, ¹H NMR, ¹³C NMR spectroscopy and mass spectrometry (Fig. S33-S46).

The UV-Vis spectrum of PQCz-T in toluene shows absorption peak at 340 nm along with shoulder peaks at 390 and 440 nm (Fig. 1a). PQCz-V exhibits similar absorption behaviour as that of T-shaped analog with a considerable enhancement of absorbance at 430 nm (Fig. 1a). The absorption spectra of the compounds in the solvents of varying polarity from toluene to dichloromethane (DCM) show no significant change in spectral shape and peak maxima (Fig. S1, S2). The substantial enhancement of longer wavelength absorption in PQCz-V can be ascribed to the facile conjugation from donor to acceptor (Sec. 3.3, ESI). The same is further corroborated through the exploration of ground state geometries using the density functional theory (DFT) at B3LYP/6-31G(d,p) level employing Gaussian 09 program package. The lowest unoccupied molecular orbitals (LUMO) of both the compounds are predominantly located on the π -electron deficient central PQ unit (Fig. 2). The HOMO in PQCz-T is mainly located in the donor unit, Cz. Whereas in PQCz-V, HOMO is distributed throughout the molecule due to the facile π -conjugation from the donor Cz to the acceptor PQ. The HOMO is more stabilized in PQCz-V and a better HOMO-LUMO overlap resulted in the intense redshifted absorption peak at 430 nm. The distinct HOMO-LUMO charge separation in the T-shaped molecule refers to the better intramolecular charge transfer (ICT) characteristics (vide infra).13



Fig. 2 The optimized ground-state HOMO and LUMO distributions and the respective energy values of (a) PQCz-T and (b) PQCz-V obtained by density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level.

The emission spectra were recorded in solvents of varying polarity (Fig. S3); the spectra in toluene and DCM are shown in Fig. 1a. The yellow fluorescence (λ_{em} = 564 nm) of PQCz-T in toluene is gradually red-shifted to 631 nm in DCM with increasing solvent polarity. Whereas, PQCz-V shows a green $(\lambda_{em} = 506 \text{ nm})$ and red $(\lambda_{em} = 606 \text{ nm})$ fluorescence in toluene and DCM, respectively (Fig. 1b). The emission maxima of both the compounds were found to be independent of the excitation wavelengths (Fig. S4). The large solvent dependent Stokes shift was observed for both the compounds. Notably, the Stokes shift in PQCz-T is higher than PQCz-V in all the solvents (Tables S1, S2), which is in agreement with the facile ICT in the former.^{2a,3} The solvent-dependent Stokes shift for both the compounds were analyzed using the Lippert-Mataga equation (Fig. S6, S7 and Table S2).^{3a,6} The salient photophysical properties as discussed above indicate a possible twisted intramolecular charge transfer (TICT) state in the former due to facile D-A rotation.14

The ICT features of the compounds were further substantiated through fluorescence quantum yield and excitedstate lifetime measurements in different solvents of varying polarity (Tables S3-S6). We observed a trend of decreasing quantum yield with increasing solvent polarity both for PQCz-T and PQCz-V. Interestingly, the quantum yields of PQCz-V is higher than PQCz-T in all the solvents. This observation is consistent with the TICT characteristics in PQCz-T contrary to the rigidification of molecular backbone due to the extended π conjugation in PQCz-V. However, the solid-state fluorescence quantum yield is higher for PQCz-T ($\Phi_f = 10\%$) compared to that of PQCz-V (Φ_f = 1.5%, Fig. S8, S9 and Table S3). The lower Φ_f in PQCz-V further supports the rigid molecular backbone amenable to π - π stacking resulting in diminished fluorescence in the solid state.4b,15 The fluorescence lifetimes of PQCz-T and PQCz-V in solvents of different polarity were found to be monoexponential (Fig. S10, S11 and Tables S4-S6). The interesting ICT characteristics encourage us to investigate further the effect of viscosity and temperature on the photophysical properties of T and V-shaped molecules.

The viscosity of the medium was varied using a binary mixture of methanol and glycerol.¹⁶ No significant change in the absorption spectra indicates that the ground state geometries of PQCzs are unperturbed with the increasing solution viscosity (Fig. S12). Interestingly, a 425-fold enhancement of

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Fig. 3 (a) The emission spectra (λ_{ex} = 340 nm) of PQCz-T (10 μ M) in solutions of methanol and glycerol with increasing percentage of glycerol (0.6 to 454 cP). (b) The photographs of PQCz-T in solutions of increasing viscosity (% of glycerol : methanol indicated) under the UV light at 365 nm.

fluorescence intensity at 630 nm was observed with the increase of viscosity from 0.6 cP to 454 cP in PQCz-T (Fig. 3a, S13). The gradual enhancement of fluorescence intensity of PQCz-T suggests the restricted rotation between the donor Cz and the acceptor PQ unit in the medium of high viscosity. Thus, the relaxation of the excited state through a lower energy weakly emissive TICT state is prevented.^{16,17} On the contrary, only a 35-fold enhancement of peak intensity was observed for PQCz-V in the same range of viscosities (Fig. S14). This observation ascertains the rigidity of the molecular backbone due to extended conjugation between Cz and PQ units in PQCz-V as discussed above (Fig. 2).

The fluorescence enhancement of PQCz-T with the increasing solution viscosity is clearly noticeable through the naked eye (Fig. 3b). Investigations with time-resolved fluorescence measurements further validate the effect of viscosity on molecular fluorescence of PQCz-T. The multi-exponential decay profiles were observed; the amplitude average fluorescence decay time increases from 23.7 to 27.5 ns with increasing solution viscosities from 24 to 454 cP (Fig. S16 and Table S9). Also, the time-resolved fluorescence anisotropy decay measurements indicate that the higher rotational correlation time is corroborating the restriction of molecular motion of PQCz-T with the increase of solution viscosity (Fig. S17 and Table S10).^{17b}

PQCz-T in THF exhibits a dramatic temperature-induced fluorochromism. The bright yellow fluorescence turns to a near white-light emission simply by increasing the solution temperature from 263 K to 338 K (Fig. 4a-c). As the temperature drops from 298 K (room temperature) to 263 K, the yellow emission band at 580 nm of PQCz-T gradually red-shifted to 610 nm with the increase in intensity (Fig. 4a). A single-component near white-light emission was observed while increasing the temperature at 328 K with the Commission Internationale de l'Eclairage (CIE) coordinates of x = 0.36, y = 0.28 (Fig. 4c). The emission is further blue-shifted with the gradual increase of temperature and a broad emission with a peak around 415 nm was observed at 338 K. The change in fluorescence color is easily distinguishable through the naked eye (Fig. 4b). The blue emission was found to be stable, and even observed upon cooling to the room temperature. The variation of short range of temperature leading to such a distinct fluorochromism covering the entire visible region, to the best of our knowledge, has not been demonstrated earlier.

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Fig. 4 (a) Fluorescence spectra (λ_{ex} = 340 nm) of PQCz-T in THF (5 µM) at different temperatures (263 K to 338 K). (b) The corresponding photographs of PQCz-T under the illumination of UV lamp (λ_{ex} = 365 nm). (c) The CIE chromaticity diagram showing the temperature-dependent luminescence color of PQCz-T in THF: (i) 263, (ii) 273, (iii) 298, (iv) 308, (v) 318, (vi) 323, (vii) 328, (viii) 333 and (ix) 338 K. (d) The plot of the ratio of fluorescence intensities at $I_{415}/(I_{415} + I_{610})$ with respect to the solution temperature.

The effect of temperature on fluorescence of PQCz-T can be further quantified by plotting the ratio of fluorescence intensities at 415 and 610 nm in the range of 263 to 330 K by the following equation (Fig. 4d). The positive temperature

coefficient (0.6 % K⁻¹) with ratiometric sensing and drastic fluorescence color change over a physiological range of temperature is promising for the development of efficient molecular thermometer.⁹ Absorption spectra of PQCz-T remain identical ruling out any decomposition at a higher temperature (Fig. S18). The concentration-dependent study also suggests that the temperature-responsive emission is not due to the aggregation of PQCz-T at higher temperature (Fig. S19). Unlike wide variation of emission color in THF, a slight blue shift and change of fluorescence intensity were observed in other solvents, like chloroform and toluene with increasing temperature (Fig. S20, S21). As evidenced in the dual-emissive TICT compounds,^{7,18} the strong temperature-dependent fluorescence of PQCz-T could be influenced by the dynamic equilibrium between LE and TICT states. The decrease in temperature stabilizes the lower energy TICT state leading to a red shift in emission. The molecular motion upon heating crosses the thermal barrier between TICT and LE states. Thus, the preferential occupation of the LE state results in a blue shift in the emission at a higher temperature.¹⁸ In contrast, the rigid D-A architecture in PQCz-V rules out the emergence of temperature-responsive emission behaviour (Fig. S22).

The radiative transition from the higher energy vibrational bands of the TICT state to the ground state upon increasing the temperature can also cause the blue shift with broad emission.^{2a} The relative rate of radiative TICT emission and nonradiative deexcitation with rising temperature may govern the fluorescence intensity.¹⁹ The multi-exponential fluorescence

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decay profile of the final blue emitting solution of PQCz-T obtained after the cooling-heating-cooling cycle compared to a single lifetime of the pristine orange fluorescent solution suggest the presence of multiple emissive species (Fig. S23, Table S11). The temperature-dependent fluorescence of D-A molecules with distinct charge separation is often attributed to thermally activated delayed fluorescence (TADF).^{1c,20} However, a continuous increase of the fluorescence intensity with temperature and reversibility over the full heating-cooling cycle is expected from an ideal TADF emitter,^{20,21} which is not the case with PQCz-T. Emission studies in THF and hexane mixture and high viscous solution of PQCz-T ascertain the temperature-responsive tunable emission in THF is not solely due to the variation of solvent polarity with temperature (Fig. S24-S26).

The ¹H NMR spectra of PQCz-T in THF-d₈ were examined to ascertain any structural change during the heating-cooling cycle. Even though the ¹H NMR spectra at different temperature remain similar (Fig. S27); a closer inspection of the aromatic region reveal a slight upfield shift of the protons with the increase in temperature (Fig. S28). Interestingly, the aromatic protons are much more resolved after the heating-cooling cycles suggesting certain structural change similar to that observed by Fu and coworkers in a phenazine-based system.²² It is likely that the pyridine moiety in PQ (acceptor) becomes nonplanar with respect to the phenanthrene unit, partially disrupting the ICT and causing predominantly the blue emission from the LE state with the increase of temperature (Fig. S29). Amidst different possible mechanisms,¹⁴ it is still challenging to pinpoint the complete molecular level picture ascribing the unique and diverse fluorescence behaviour of PQCz-T (Fig. S31, S32). The present communication lays the foundation towards the future exploration of rich photophysical attributes of PQbased molecular probes.

In conclusion, we fabricated a new class of T and V-shaped D-A-D type molecules employing pyridoquinoxaline as acceptor and carbazole as donor units. The subtle variation of the molecular shape and ICT characteristics were found to be responsible for the polarity-dependent tunable emission across the visible region in PQCz-T and PQCz-V. PQCz-T exhibits environment-sensitive fluorescence with large Stokes shift, strong red emission in the solid state and a drastic enhancement of fluorescence with the increase of viscosity of the medium. A dramatic change of temperature-induced fluorescence color in PQCz-T led to tunable emission covering the entire visible region including a single-component near white-light emission. Such diverse optical properties exhibited by PQCz-T is rarely observed in a single molecular platform (Table S12). The current study reveals a design strategy opening up new avenues for the development of multifunctional materials based on pyridoquinoxaline promising for optoelectronics, sensing and imaging in biological medium. Financial support from BRNS, DAE (no. 37(2)/14/06/2016-BRNS/37020) and infrastructural support from IISERB are

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