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Two novel donor-acceptor systems (F10C-PTZ and F10C-DPQ) were designed and synthesized, in which corrole is an acceptor and either phenothiazine (PTZ) or 2,3-di(2-pyridyl)quinoxaline(DPQ) are energy/electron donors. These dyads represents one of the few examples of photostable corrole dyads reported in the literature, but the first example of 2,3-di(2-pyridyl)quinoxaline(DPQ) containing meso substituted corrole (F10C-DPQ) also directly connected PTZ to meso position of corrole (F10C-PTZ). Both the dyads were characterized by high-resolution mass spectrometry (HR-MS), NMR (¹H, ¹³C, ¹⁹F), UV-Vis, Study state Fluorescence, Time-resolved fluorescence (TCSPC, MCP-PMT), electrochemical methods (CV, DPV) as well as theoretical calculations (DFT, TD-DFT). Absorption and electrochemical studies evident that, there exist minimum π - π interactions between two hetero chromophoric units in the dyad. The steady state fluorescence studies indicate an efficient quenching of emission corresponding to PTZ unit in F10C-PTZ dyad is attributed to singlet–singlet energy transfer from PTZ to corrole. In addition to the spectral overlap, excitation spectra provided additional evidence for intramolecular energy transfer. Whereas in F10C-DPQ dyad, the reductive electron transfer, from ground state of DPQ to excited state of corrole was observed. Negative free energy (Δ G) for charge separation, anodic shift of reduction potential of corrole and frontier molecular orbital (LUMO) location providing addition support for charge transfer. The solvent dependent rate of an energy and electron transfer was discussed.

1. Introduction

Natural Photosynthesis is a physiological-biochemical process in which the solar energy can be converted to the chemical energy.¹ Harvesting of Sunlight by antenna complexes surrounding the reaction center represents the first step of the natural photosynthesis performed by plants, algae and cyanobacteria. The complex of proteins and pigments embedded in the thylakoid membrane is composed by carotenoids and (B)Chls, which are responsible for light absorption, the captured light energy by the antenna exhibit remarkable transport properties, which facilitate highly efficient excitation energy transfer (PEnT) across the long distances via a cascade of radiationless energy-transfer steps and subsequently conveyed to the reaction center through resonant energy transfer mechanisms, where the charge separation occurs. This excited energy is necessary to perform (uphill process) such a demanding step is water spilling in oxygenic photosynthesis, as a result, the light-harvesting machinery must produce four electrons for further processes.²⁻⁵ In addition to energy transfer, electron transfer also considered as important chemical reaction, as an

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elementary chemical process, it constitutes a key step in biological processes of enormous relevance to life.⁶ Thus, identifying working principles that could serves as blueprints for the design of nature inspired devices is an active area of research for the development of future scalable technologies.⁷

In order to elucidate the complex events in energy transfer process and to achieve the long lived charge separated (CS) state, much effort has been devoted to the construction of artificial photosynthetic model systems.^{8,9} In spite of the fact that, the substantial progress has been achieved in this area, research towards exploring for new models that differ from existing systems in photosensitizer, spacer and position of substitution etc..., are in large demand because of their applications in many scientific fields for example materials chemistry,¹⁰ biochemistry,¹¹ photodynamic therapy,¹² catalysis,¹³ DSSC.¹⁴ To mimic the key steps in the natural process, e.q. Photo-induced electron (PET) and energy (PEnT) transfer processes, researchers choose to use entities that have great resemblance to natural systems both in terms of structure and properties.¹⁵ Porphyrin and its analogues tetrapyrrole, *i.e.*, corrole proved to be potent candidates for this purpose, because of their similarities with chlorophyll.¹⁵ Porphyrin sensitizers appear to be monopolies of the study due to their low cost, smooth synthetic methods, easily tunable electrochemical and photophysical properties by substituting different functional groups at their $\boldsymbol{\beta}$ and/or meso position.¹⁶ Corroles are tetrapyrrole analogues of porphyrin with a direct pyrrole-pyrrole linkage and three meso carbons, the lack of one methine (=CH-) bridge is responsible for the lower symmetry, higher fluorescence quantum yields, lower oxidation potentials and more intense absorption in the low energy

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region of visible spectrum. However corroles are poorly explored as compare to porphyrin due to their synthetic challenges and moderate stability.¹⁷ After the synthetic breakthroughs by Gryko, Gross and Paolesse,¹⁸ scientific community quest for stable chromophores that comprise of corrole and other units is on-going research. It is important to mention that the corrole core might be electron withdrawoing stabilized hv groups like petaflourobenzaldehyde at their meso position,¹⁹ by cosidaring this property there are some stable donor-acceptor (D-A) systems have been reported, however most of them are constituted with the electron accepting moiety's, for example fullerene²⁰ and imide derivatives.²¹ On the other hand the energy/electron donor groups like coumarin²² and bodipy²³ have been reported but donor entities with stable corrole core are relatively low in the literature.

Phenothiazine (PTZ) is a tricyclic heteroaromatic chromophores, have strong tendency to donate electrons than their counter analogs such as triarylamines and carbazole chromophores, due to the presence of both electron-releasing nitrogen and sulphur atoms.²⁴ In addition to this. PTZ have gained much attention, due to their interesting structural features is that, the torsion angle around the N-S axis (147.10) of the PTZ ring attains bowl-shaped (nonplaner butterfly) conformation, which forbids the molecular aggregation, which in turn, prevents the formation of intermolecular excimer even in highly concentrated solution and solid state.²⁵ By encasing these points PTZ have been employed in development of various applications such as bulk heterojunction solar cells (BHSCs),²⁶ dye-sensitized solar cells (DSSCs)²⁷ and organic light emitting diodes(OLED).²⁸ There are many donor-acceptor small molecules based on PTZ have been reported,²⁹ but so far combination with corrole is very few,³⁰ this might be due to the instability of the composed dyads comprise of corrole and donor entities(vide infra).

contain planar π -conjugated aromatic rings, in which aggregation $[M+1]^+$. leads to fluorescence quenching due to non-radiative deactivation.³⁴ The molecules which are shows AIEE is of current interest because their utilities in the development of OLEDs,³⁵ organic field effect transistors (OFETs)³⁶ and sensors.³⁷ The same group investigated its fluorescent sensor behavior of DPQ, based on the p^H value for the detection of acidic and basic medium.³¹ Jia et al

reported D-A system based on tetrathiafulvalene and DPQ.³⁸ In addition to AIEE and sensor properties (beyond the scope of this publication), DPQ shows relatively low oxidation potential (0.61 V vs Ag/Ag⁺) might be the suitable as an electron donor in model compounds for artificial charge separation and molecular electronic devices. The advantage of DPQ over the other electron donors is that: (1) there is no heavy-atom effect (like ferrocene) which means there no formation of triplet state of DPQ via Intersystem crossing (ISC) (2) availability two extra binding sites even after covalently connecting to counter moiety. These properties turned our attention to utilization of this ligand for construction of dyads.

One of the important and unique propertie of corrole is, the role of either an energy/electron donor or acceptor depends on the nature of counter entities. Introducing pentafluorophenyl units at 5 and 15 positions, the corrole core secure good photostability for investigation of photophysical characterization (vide infra). All these keeping in mind we have synthesized two new dyads based on PTZ (F10C-PTZ) and 2,3-di(2-pyridyl)quinoxaline (F10C-DPQ), In which, PTZ/DPQ are an energy/electron donor and corrole as an acceptor and we have also explored the effect of solvent polarity on the rates of photoinduced energy and electron transfer in these dyads.

2. Experimental

2.1. Synthesis of precursors

Synthesis of 10-methyl-10H-phenothiazine-3- carbaldehyde (PTZ-2-perfluorophenyl (1H-pyrrol-2-yl)methyl)-1H-pyrrole CHO), (DPM),³⁹ both the dyads F10C-PTZ and F10C-DPQ was synthesized according to reported and a bit modified procedures.

2.2. 6-bromo-2,3-di(pyridin-2-yl)quinoxaline(DPQ-Br): DPQ-Br was synthesized according reported and slightly modified procedure⁴¹. 4bromobenzene-1,2-diamine (50 mg, 0.270 mmol) and 1,2-2,3-bis(2-pyridy1)quinoxaline (DPQ), in which two pyridyl units are di(pyridin-2-yl)ethane-1,2-dione (65 mg, 0.306 mmol) were dissolved attached to the 2 and 3 positions of the guinoxaline moiety through in ethanol (15 ml). The suspension was stirred and refluxed for 3a single bond. The coplanar arrangement of these two pyridine hours under inert atmosphere. Reaction mixture cooled to room rings with quinoxaline groups is impossible, due to steric forces temperature and ethanol was removed by distillation under reduced between protons that are close proximity to each other when the pressure. The resulting crude product was directly purified by silica two pyrinde rings attains planar geometry. To avoid this steric gel chromatography (100-200) with CH2Cl2/MeOH (10:1) used as hindrance the two pyridyl groups prefers to attain a twisted eluent, and the first yellow-orange band was collected. After geometry with the 140° out of plane of the quinoxaline ring.³¹ DPQ recrystallization from CH₂Cl₂ and hexaneDPQ-Br was obtained as is structurally related to pyrazine and 2,2'-bipyrimidine, their metal yellow solid (yield 90%).¹H-NMR (400 MHz, CDCl3) δ (ppm): 8.32 (d, 1H, complxes are well studied,³² the chelating properties of DPQ with J = 1.9 Hz), 8.27 (s, 2H), 8.01 (d, 1H, J = 8.9 Hz), 7.88 (t, 2H, J = 7.37 Hz 3d, 4d and 5d transition metal cations also reasonably studied.³³), 7.80 (dd, 1H, J' = 1.99 Hz, J'' = 2.02 Hz), 7.73 (t, 2H, J = 5.71 Hz), 7.16 However the structure-property relation of this ligand is much (t, 2H, J = 5.06 Hz). ¹³C-NMR (CDCl3) δ : 157.10, 156.98, 153.16, attracting, recently Ajay Misra et al. reported that the restriction of 152.73,148.57, 148.54, 141.67, 139.83, 136.76, 136.66, 134.04, 131.64, intramolecular rotation of two pyridyl groups in their aggregataion 130.62, 124.51, 124.24, 124.16, 123.19, 123.13. Anal. Calcd for state, which will lead to the aggregation induced emission $C_{18}H_{11}BrN_4$: C, 59.52; H, 3.05; N, 15.43; found C, 59.51; H, 3.03; N, enhancement (AIEE),³¹ in contrast to the most organic fluorophores 15.44. ESI-Mass calcd for $C_{18}H_{11}BrN_4$: m/z = 363.21, found m/z = 364.10

> 2.3. 2,3-di(pyridin-2-yl)quinoxaline(DPQ-Control compound): This compound was synthesized by an analogous manner of the preparation of DPQ-Br, in which, benzene-1,2-diamine was used instated of its bromo-derivative. (yield 92%). ¹H-NMR (400 MHz, CDCl3) δ (ppm): 8.39 (d, 2H, , J = 4.5 Hz), 8.27-8.21(q, 2H, J = 3.5

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Hz), 7.97 (d, 2H, J = 7.8 Hz), 7.85-7.79 (m, 4H), 7.27-7.22 (q, 2H, J = 7.25 Hz). 13C-NMR (CDCl₃) δ : 157.35, 152.46, 148.66, 141.07, 136.70, 130.53, 129.39, 124.23, 122.94. Anal. Calcd for C₁₈H₁₂N₄: C, 76.04; H, 4.25; N, 19.71; found C, 76.02; H, 4.24; N, 19.73. ESI-Mass calcd for C₁₈H₁₂N₄: m/z = 284.31, found m/z = 284.11 [M]⁺.

2.4 4-(2,3-di(pyridin-2-yl)quinoxalin-6-yl)benzaldehyde(DPQ-

CHO): DPQ-CHO was synthesized according to reported and slightly modified procedure.⁴² DPQ-Br (100 mg, 0.276 mmol), 4formylphenylboronic acid (180 mg, 1.2 mmol) and Pd(PPh₃)₄ (30 mg, 0.026 mmol) was charged in a two necked round bottomed flask equipped with condenser and nitrogen adaptor, then the reaction flask was degassed with nitrogen for 10 min. The predegassed dry tetrahydrofuran (20 ml) and 2 M Na₂CO₃ aqueous solution (3 ml) was added into the reaction mixture and heated to reflux with continuous stirring in the dark for 8 h, under the nitrogen. After cooling to room temperature, the organic layer was separated and the aqueous layer was extracted with CH_2CI_2 . The combined organic layer was washed with water, brine, and dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography eluting with CH2Cl2/MeOH (10:2), the title compound was obtained as pale-yellow solid (yield, 75%).¹H-NMR (400 MHz, CDCl₃) δ (ppm): 10.05 (s, 1H), 8.43 (d, 1H, J = 6. 40 Hz), 8.32 (d, 1H, J = 4.20 Hz), 8.25 (d, 1H, J = 9.42 Hz), 8.04 (dd, 1H, J' = 2.10 Hz, J" = 1.79 Hz), 7.99-7.87(m, 4H), 7.77(t, 2H, J = 7.8 Hz), 7.62-7.55(q, 1H, J = 7.1 Hz), 7.50-7.36(m, 2H), 7.19(t, 2H, J = 5.4 Hz). $^{13}\text{C-NMR}$ (CDCl) $\delta:$ 191.70, 157.20, 153.19, 152.82,148.61, 145.53, 141.66, 141.25, 140.94, 136.66, 135.93, 132.16, 132.04, 131.97, 130.51, 130.10, 129.82, 128.60, 128.45, 128.14, 127.66, 124.32, 124.23,123.16. Anal. Calcd for C25H16N4O: C, 77.30; H, 4.15; N, 14.42; found C, 77.29; H, 4.13; N, 14.45. ESI-Mass calcd for C H N O: m/z = 388.42, found m/z = 388.45 [M]⁺.

2.5 Synthesis of corrole-DPQ dyad (F10C-DPQ):

Pentafluorophenyl- dipyrrylmethane (DPM) (320 mg, 1.025 mmol) and DPQ-CHO (200 mg, 0.512 mmol) were dissolved in MeOH (80 ml), Concentrated HCl_{aq} (5 ml) in water (80 mL) was then added, and the resulting suspension was stirred at room temperature for 1 h. The reaction mixture was extracted with CH_2Cl_2 (2 × 50 mL), and the organic phase was washed with water (3 ×50 ml) and dried over anhydrous Na₂SO₄, and concentrated to 50 ml volume then 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (280 mg, 1.25 mmol) was added, then the mixture was vigorously serried for 15 minutes at room temperature. DDQ was removed by washing coloumn through the silica gel (100-200) chromatography with CH₂Cl₂ as eluent. The resulting crude compound was further purified by silica gel chromatography (300-400) with CH₂Cl₂/MeOH (10:1) used as the eluent. The title compound was obtained as a dark violet solid after recrystallization from CH₂Cl₂ and hexane (yield 34%) H-NMR (400 MHz, CDCl₃) δ (ppm): 9.11(d, 2H, J = 4.1 Hz), 8.79 (dd, 4H, J' = 4.6 Hz, J" = 6.5 Hz), 8.57 (d, 2H, J = 3.52 Hz), 8.38 (dd, 6H, J' = 12.03 Hz, J" = 7.84 Hz), 8.22 (d, 2H, J = 7.83 Hz), 8.03 (d, 2H, J = 7.69 Hz), 7.86 (t, 2H, J = 7.35 Hz), 7.29 (t, 3H, J = 8.01 Hz), -2.51 (s, 3H). ¹⁹F-NMR $(CDCl_3) \delta(PPM)$: -138.72(dd, 4F, J' = 16.7 Hz, J'' = 5.6 Hz), -152.56 (t, 2F, J = 20.9 Hz), -161.61 (m, 4F). ¹³C-NMR (CDCl $\lambda \delta$: 157.33, 152.89, 152.30, 148.63, 147.26, 144.88, 142.73, 141.63, 141.46, 140.68,

138.82, 136.59, 135.48, 130.20, 130.03, 128.91, 128.15, 127.72, 127.04, 126.45, 125.67, 125.16, 124.14, 122.95, 117.48, 112.71. Anal. Calcd for $C_{55}H_{26}F_{10}N_8$: C, 66.80; H, 2.65; N, 11.33; found C, 66.78; H, 2.60; N, 11.30. HRMS calcd for $C_{55}H_{26}F_{10}N_8$: m/z = 988.2121, found m/z = 989.2215 [M+1]⁺.

Synthesis of corrole-PTZ dyad (F10C-PTZ): The similar 2.6. synthetic procedure (F10C-DPQ) was adapted to preparation of the dyad, in which PTZ-CHO was used instead of DPQ-CHO. (yield 31%). 1H-NMR (400 MHz, CDCl3) δ(ppm): 9.08 (d, 2H, J = 4.2 Hz), 8.71 (dd, 4H, J' = 4.72 Hz, J'' = 12.01 Hz), 8.55 (d, 2H, J = 3.01 Hz), 7.94 (d, 2H, J = 8.94 Hz), 7.23-7.14 (m, 3H), 6.99-6.91 (q, 2H, J = 7.65 Hz), 3.61 (s, 3H),-2.48 (s,3H). 19F-NMR (CDCl3) δ(ppm): -137.74 (dd, 4F, J = 21.4 Hz), -153.12 (t, 2F, J = 18.8 Hz), -161.77(m, 4F). 13C-NMR (CDCl3) δ: 145.78, 145.68, 139.36, 135.67, 133.92, 132.92, 127.73, 127.69, 127.39 ,123.27, 122.74, 122.59, 122.44, 121.53, 114.34, 113.03, 112.29. Anal. Calcd for C44H21F10N5S: C, 62.78; H, 2.51; N, 8.32; S, 3.81 found C, 62.77; H, 2.49; N, 8.30; S, 3.79. HRMS calcd for $C_{44}H_{21}F_{10}N_5S$: m/z = 841.1358, found m/z =842.1440 [M+1]⁺.



Fig. 1. Synthetic scheme of dyads along with their monomers.

3. Results and discussion

3.1. Synthesis and structure characterization

Fig.1. illustrates the synthesis of both the dyads (F10C-DPQ and F10C-PTZ) including their formyl derivatives of hetero aromatic hydrocarbons (PTZ-CHO and DPQ-CHO). There are two main synthetic strategies for meso-substituted corrole dyads: (1) the synthesis of corrole core molecule first, followed by the modification of the peripheral groups; (2) the preparation of the desired formyl derivative, which is then used in a condensation reaction to produce the corrole dyad. On the basis of the results of previous reports, ²⁰⁻²³ we have fallowed the second strategy because of the moderate stability of corroles.

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Preliminary characterizations of both the dyads were carried out by HRMS and UV-Vis spectroscopic methods. The HRMS spectrum of both the dyads F10C-DPQ and F10C-PTZ showed peaks at m/z = 989

 $([M+1]^{+}, C_{H}, F_{N}, N)$ and m/z = 842 $([M+1]^{+}, C_{H}, F_{N}, N, N)$, are ascribable to the molecular-ion peak (supporting information, Fig. S1- S4). ¹H, ¹⁹F and ¹³C-NMR spectra of both the dyads including their constituent monomers are presented in the ESI (Fig. S5-S16) In the F10C-PTZ dyads the presence of the singlet corresponds to N-methyl group of PTZ at 3.61 ppm indicating the incorporation of PTZ unit with corrole. The presence of extra six signals (from 8.62- 7.2 ppm) in ¹H-NMR of F10C-DPQ indicating the incorporation of DPQ unit with corrole (see experimental section).

3.2. UV-Vis Spectroscopy

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The optical absorption spectra of the dyads along with their constituent monomers in CH₂Cl₂ solvent are shown in Fig. 2. Wavelength of maximum absorption (λ_{max}) and molar extinction coefficients (\mathcal{E}) are summarized in Table 1.



Fig. 2. Optical absorption spectra of the dyads along with their monomers in $\mathsf{CH}_2\mathsf{Cl}_2.$

The absorption spectra of corrole (Soret band around 420 nm and Q-bands around 500-670 nm) can be interpreted in the frame of "four-orbital model".⁴³ The absorption bands of the pristine PTZ shows two peaks at 253 and 310 nm in CH₂Cl₂ arising from localized aromatic π - π * transitions,⁴⁴ the pristine DPQ shows bands at 246, 271 and 335 nm in CH₂Cl₂ arising from intraligand π - π * transitions of the quinoxalin and pyridine rings.⁴⁵ The absorption spectra of

both the dyads are mere superposition of the absorption spectra of constituent monomers, in which the absorption bands around 272 nm in F10C-DPQ dyad and 253 nm in F10C-PTZ dyad corresponding to DPQ and PTZ respectively. The incorporation of the PTZ/ DPQ at the meso-position of the corrole results in the following changes in the absorption spectra in both the dyads: (i) red shift (4-5 nm) and splitting of the Soret bands; (ii) red shift (8-10 nm) of Q-bands; The red shift might be due to extending electron delocalization thus leads to ground state stabilization and the splitting of Soret band is due to bulky substitution at meso position. The more red shift of Qbands over the Soret band in both the dyads might be due higher steric hindrance felt by periphery of the macrocycle, our results also in line with the litarature.⁴³ When we compare the absorption spectra of the F10C-PTZ (PTZ is directly connected to meso-position of corrole core) with earlier reported TPC-PTZ (PTZ is connected via vinylic spacer at β -pyrrolic position of corrole) $^{30(a)}$, in which both the Soret and Q-bands are red shifted almost double to the F10C-PTZ, this might be due to more extending conjugation in TPC-PTZ

3.3. Electrochemistry

In order to confirm the magnitude of the coupling in both the dyads and to evaluate the redox potentials which are useful for the interpretation of the site of electron transfer of the individual redox units, we have carried out differential pulse voltammetry (DPV) and cyclic voltammetry (CV) experiments. Fig. 3, depicts the differential pulse voltammograms of both the dyads along with their constituent monomers. All the experiments were carried out under the same experimental conditions, 0.1 M TBAPF₆ used as supporting electrolyte in dry DCM under N₂ atmosphere, the redox data are summarized in Table 1.



Fig. 3. Differential pulse voltammograms dyads along with their constituent monomers in CH_2Cl_2 containing 0.1M TBAPF₆, with scan rate 100 m Vs⁻¹.

From CV and Fig. 3. it is evident that the F10C-DPQ dyad exhibits three oxidations and three reductions, in which second oxidation and second reductions are reversible (i_{pc}/i_{pa} 1, ΔE_p = 65±3 mV). whereas F10C-PTZ shows four oxidations and two reductions in which first two oxidations and second reductions are reversible and remaining are quasi-reversible ($E_{pc}-E_{pa}$ =95 -160 mV). The pristine DPQ shows two quasi-reversible oxidations at ($E_{1/2}$ = 0.62 and 1.88

V vs Ag/Ag⁺) and one reversible reduction at (E $_{1/2}$ = -1.68 V), the pristine PTZ shows one reversible oxidation at $(E_{1/2} = 0.76 V)$ fallowed by one quasi-reversible oxidations at (E $_{1/2}$ =1.46 vs Ag/Ag⁺) and there is no reduction was observed corresponding to PTZ within the experimental window (0 to -2 V), our results are in line with the literature.⁴⁴ The first oxidation/reductions of the dyads only important to understand the charge transfer states (E_{CT}). In both the dyads the first oxidation is corresponding to donor entity and second oxidation corresponding to corrole moiety. Interestingly the DPQ oxidation was found to be easier by 80 mV in F10C-DPQ dyad, whereas in F10C-PTZ dyad, there was no anodic and cathodic shifts of redox potentials corresponding to either PTZ or corrole was observed. Collectively, ¹H NMR, UV-Vis and electrochemical data indicate that there are no significant electronic interactions between the hetero chromophores in these dyads. This allows an approach based on selective excitation of the individual subunits to exploit the excited state properties of the dyads.

 Table 1. UV-Visible and Electrochemical Data of tpfc (5,10,15tris(pentafluorophenyl)corrole) DPQ,PTZ, F10C-DPQ and F10C-PTZ.

 Absorption, λ_{max} nm (log ε, M⁻¹ cm⁻¹)^a

 Potential V vs Ag/Ag^{+b}

Compound	Corrole bands	PTZ / DPQ- Bands	Oxidation	Reduction
tpfc	299 (4.21) 407 (5.12), 420(5.03), 561(4.35), 604(4.06)	-	0.86, 1.02, 1.73	-0.79, -1.62
DPQ	-	246(4.41), 271(4.20), 335(3.8)	0.62, 1.88	-1.68
PTZ	-	251(4.33), 310(3.75)	0.75, 1.46	-
F10C-PTZ	411(4.86),426(4.8), 518(3.79) ^C 563(4.09),614(3.86)	253(4.43),303(4.16)	0.76,1.0, 1.35, 1.61, 1.84	-0.78, -1.69
F10C-DPQ	412(4.93), 424(4.88),517(3.80) ^C ,563(4.09),612(3.90)	274(4.54), 338 (4.10) ^c	0.54, 0.88, 1.78	-0.70 , -1.49, -1.69

^aSolvent CH₂Cl₂. Error limits: λ_{max} , ±1 nm; log ϵ , ±10%. ^bCH₂Cl₂, 0.1 M TBAPF₆ Glassy carbon working electrode; standard Ag/AgCl is reference electrode, Pt electrode is auxiliary electrode. Error limits, $E_{1/2} \pm 0.03$ V. ^cShoulder peak.

3.4. Computational studies

The theoretical studies involving DFT and TD-DFT calculations using B3LYP/6-31G (d, p) level were executed to visualize the geometry, electronic structure and optical properties of the dyads. The optimized structures, molecular electrostatic potential maps (ESP) and frontier molecular orbitals (HOMO and LUMO) are shown in Table 2. From the ESP maps of both the dyads it is evident that, the positive potential (blue colour) was located on donor entity and inner-corrole core, the negative potential (yellow-red) was located on outer-corrole core, especially on electron withdrawing pentafluoro phenyl groups. By careful examination of the ESP map of F10C-DPQ dyad, the negative potential located on pyridyl and quinoxaline nitrogen providing additional evidence for the capture of metal cations.³⁸ It is important to mention that, there are eight energy minima conformations possible for F10C-DPQ dyad due to the different possible orientations of the pyridines. Among them the lowest energy minima, in which two pyridyl nitrogens are oriented away from the center (out-out conformation) was taken into an account.³⁸ By careful examination of frontier molecular orbitals of both dyads, the HOMO-1 and HOMO distributed among the donor subunits (PTZ/DPQ) and corrole, whereas LUMO was completely located on the acceptor corrole. Based on electron density distributuions on HOMO and LUMO, we can describe these dyads are perfect donor-acceptor systems, in which PTZ/DPQ are donor entitys and corrole is acceptor entity. The gas phase HOMO-LUMO gap, edge-to-edge distance (Re-e), center-to center distance (R_{c-c}) between corrole and DPQ/PTZ units in the dyads were summarized in Table 3.

Based on the experimental observations, TD-DFT studies of these dyads were carried out by using same basis set in order to gain a deeper understanding of the excited-state transitions within the framework of the polarizable continuum model (PCM) in CH_2CI_2 as the solvent. Theoretical absorption spectra of F10C-DPQ and F10C-PTZ have been computed from the frontier molecular orbitals by using the GaussSum -2.1.6. Software and plotted (supporting

Information Fig. S17). A closer look at the transitions involved in the closer look at the transitions involved in the computation of absorption bands revealed that the Soret band (Bband) of the F10C-DPQ consisted of two main transitions bellow 450 nm and Q-band consisted of single low energy transition bellow 610 nm, whereas in case of F10C-PTZ, the Soret band (B-band) consisted of three main transitions and Q-band consisted of single low energy transition bellow 610 nm. similar to F10C-DPQ. When we compare the theoretical absorption of the both the dvads, we did not find much difference in terms of wavelength and oscillator strength but there is a high energy transition with low oscillator strength was observed bellow 310 nm in F10C-PTZ, this might be due to π - π * transition of the PTZ, whereas we did not find any high energy transition corresponding to DPQ in F10C-DPQ. When we look into the contributions of the calculated transitions, the B-band of the F10C-PTZ constituted by HOMO-1→LUMO+1 major transition (43%), whereas in the F10C-DPQ dyad, the B-band constituted by HOMO \rightarrow LUMO+2 (58%). The dominant contribution for Q-band transitions (low energy) bellow 610 nm for the both dyads are similar. In case of F10C-DPQ dyad, the major transition constituted by an HOMO→LUMO (78%), in case of F10C-PTZ, the major contribution is HOMO \rightarrow LUMO (86%), the remaining contributions are much less significant. When we compare the theoretical absorption maxima of the both the dyads, a slight red shift in the absorption maxima (406 nm) of F10C-DPQ was observed compare to F10C-PTZ (399 nm). The computed wavelength positions are in reasonable agreement with the experimental values. Wavelength of absorption maximum (λ max), excited state energy (E), oscillator strength (f) and percentage contribution of molecular orbital of both dyads by means of absorption spectra are shown in Table S1.

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Table 2. Energy minimized optimized structures, FMO's and Electrostatic potential maps (ESP) of F10C-PTZ and F10C-DPQ dyads. Table 3. Optimized distances between corrole and PTZ/DPQ moieties and F100 DT7

related orbital energy's (eV) in the E10C-PT7 and E10C-DPO dyads

	1100112	1100 01 Q
Optimized structure	A A A A A A A A A A A A A A A A A A A	the part
Electrostatic potential map (ESP)		de la constante de la constan
LUMO+1		
LUMO		
номо		
HOMO-1		

3.5. Study-state fluorescence studies

3.5.1. Selective excitation of donor entity (PTZ/DPQ), Singletsinglet energy transfer from PTZ to corrole: Unlike the ground state properties, we observed major differences in singlet state properties of the dyads when compared to their monomeric units. When selectively excitation at 310 nm of equimolar (10^{-6} M) solution of the F10C-PTZ dyad and its constituent monomer (PTZ) in dichloromethane (where the PTZ moiety absorbs predominantly), the emission maxima (450 nm) corresponding to PTZ was completely quenched, when compare to pristine PTZ see Fig. 4.

	F10C-PTZ	F10C-DPQ	
E, K.cal/mol	-2108117	-2226246	
$R_{e-e}^{}, A^{o}$	5.22	10.53	
R _{c-c} , A ^o	8.30	12.89	
HOMO-1	-5.24	-5.35	
номо (н)	-4.95	-5.07	
LUMO (L)	-2.58	-2.62	
LUMO+1	-1.96	-2.09	
H-L gap	2.37	2.45	

Emission maxima and fluorescence quantum yields were collected in Table 4. By careful examination of absorption and emission spectra's (Figs. 2 and 4), it is found that there exist a strong overlap between PTZ emission and corrole absorption, clearly suggesting that the quenching of fluorescence emission of PTZ in F10C-PTZ dyad can be due to intramolecular photoinduced energy transfer from excited singlet state of PTZ to corrole(¹PTZ*-corrole \rightarrow PTZ-¹corrole*). Similar results were also observed when we performed the same experiment in different solvents (PhMe, MeCN and DMF) with varying polarity. It is important to mention that the emission corresponding to PTZ in F10C-PTZ dyad completely guenched in all the investigated solvents, in contrast to TPC-PTZ dyad (donor PTZ connected via vinylic spacer at β -pyrrolic position of corrole) reported by us earlier,^{30(a)} where the quenching is more pronounced in non-polar solvents then the polar solvents. The complete quenching of PTZ emission in F10C-PTZ dyad might be due to very close proximity of donor-acceptor entities (without any spacer between the D-A), which facilities the easier migration of exciton, similar results (complete quenching of donor emission in dyad) was observed in corrole-coumarin dyads,²² Carbazole-Benzothiadiazole⁴⁶ and PTZ-malononitrile⁴⁷ donor-acceptors systems. By careful examination of Fig. 4. It is understand that PTZ emission was guenched and appearance a new emission band corresponding to corrole (652 nm), it is clearly evidenced that, intramolecular energy transfer from PTZ to corrole in F10C-PTZ _dyad. In order to provide further evidence for the intramolecular energy transfer, we have performed similar experiments with 1:1 mixture of PTZ with corrole, these controlled experiments shows that there is no effect on the emission intensity of PTZ (no quenching), and extending the emission scan to the corrole emission region revealed no emission corresponding to corrole, suggesting no energy transfer from the excited PTZ under intermolecular conditions. Furthermore the excitation spectrum of F10C-PTZ recorded by setting the emission monochromator to corrole emission (652 nm) is well matched with absorption spectrum of the dyad, providing further evidence for the intramolecular energy transfer Fig. 5.



Wavelength (nm) Fig. 4. (a) Emission spectra of PTZ, F10C-PTZ at (λ_{ex} = 310 nm) (b) Emission spectra of dyads along with pristine corrole (λ_{ex} = 420 nm) in CH₂Cl₂ equi-absorbing solutions (O.D. λ_{ex} = 0.05), the sharp peaks labelled with asterisk (*) is due to instrument response.



Fig. 5 Overlay of excitation spectra with absorption spectra of TPC-PTZ (λ_{em} = 652 nm) in dichloromethane, the excitation spectra was normalized with respect to the absorption spectra. The sharp peaks labelled with asterisk (*) is due to instrument response.

The E_{0-0} (0-0 spectroscopic transition energy) values of the PTZ (3.20 eV), corrole (2.10 eV) entities in the dyads were estimated from an overlap of their absorption and emission spectra. From the extent of the fluorescence quantum yields, the quenching efficiency (Q) can be estimated from eq. (1) and rate of fluorescence quenching k_{obs} estimated from eq. (2) in all the investigated solvents and data are listed in (Table 4 and 5).

 $Q = [\Phi(ref) - \Phi(dyad)]/\Phi(ref)$ (1)

 $k_{obs} = [Q/(1-Q)]/\tau_{(ref)}$ (2)

In equation (1) and (2) $\Phi(ref)$ and $\Phi(dyad)$ refer to the fluorescence quantum yields of PTZ and dyad. $\tau_{(ref)}$ is the excited singlet state life time of pristine PTZ (1.45, 1.68, 1.76, 2.10 ns in CH₂Cl₂,PhMe, MeCN and DMF respectively). From Table 4, the quenching efficiency of the F10C-PTZ dyad was more efficient in all the investigated solvents (99%). Apart from this, we did not found emission corresponding to even pristine DPQ, in all the investigated solvents, our results also in agreement with the previous reports. $^{31,\,38}$

In order to shed more light on the mechanistic explanation of the energy transfer occurring in the F10C-PTZ dyad, we can take advantage of well-established models for energy transfer. Energy transfer between singlet states can occur by two different mechanisms; (1) dipole-dipole interaction (Forster mechanism) (2) electron-exchange mechanism (Dexter mechanism). When strongly emitting donors (as the PTZ) and strongly absorbing acceptors (as the corrole) are involved, the mechanism is generally of the Forster Whereas in case of poorly emitting state of donors, Dexter type. mediated energy transfer prevails. In addition to this, the perfect overlap of excitation spectra with absorption spectra of the dyad (Fig. 5) providing further evidence for the energy transfer via a Forster mechanism.^{21(a)} It is important to mention that, irrespective of mechanisms, the rate of energy transfers proportional to extent of spectral overlap (J) of the donor emission with acceptor absorption. The rate of energy transfer (k_{Forster}) from PTZ to corrole can be calculated by means of eq. (3).

$$k_{Forster} = (8.8 \times 10^{-25}) \kappa^2 \Phi_D J_{Forster} \eta^{-4} \tau_D^{-1} R_{DA}^{-6}$$
(3)

Where Φ_D and τ_D are the emission quantum yield (Table 4) and lifetime of the pristine PTZ, R_{DA} is the donor-acceptor centre-to-centre distance (Table 3), η is the refractive index of the employed solvent and $J_{Forster}$ is the overlap integral, K^2 the orientation factor (2/3) for the randomly oriented donor-acceptors (*vide infra*). The spectral overlap integral, $J_{Forster}$ can be evaluated according to eq. (4).

$$J_{Forster} = \int F_{D}(\lambda) \mathcal{E}_{A}(\lambda) \lambda^{4} d\lambda / \int F_{D}(\lambda) d\lambda \qquad (4)$$

Where $F_D(\lambda)$ is the fluorescence intensity of the donor, $E_A(\lambda)$ molar extinction coefficient of the acceptor expressed in units of M^{-1} $\ cm^{-1}$

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Table 4. Emission properties of the dyads along with their monomer.

	$\lambda_{em} nm(\Phi, \% Q)^a \qquad \lambda_{ex} = 420 nm$			
Compound	CH ₂ Cl ₂	PhMe	MeCN	DMF
tpfc	637(0.137)	64(0.13)	618(0.809)	621(0.719)
F10C-PTZ	650(0.054,60)	655(0.082,36)	632(0.344,57)	635(0.362,49)
F10C-DPQ	653(0.062,55)	649(0.072,44)	653(0.016,98)	638(0.0097,98)

^a Spectra were measured at RT, Error limits $\lambda_{em} \pm 1$ nm, $\Phi \pm 10\%$. The quantum yields of the dyads were estimated by a comparative method using tpfc ($\Phi_f = 0.13$) in toluene as a standards.²² The PTZ quantum yields were determined against quinine sulphate in 0.1 N H₂SO₄ ($\Phi = 0.546$) as the standard ($\lambda_{ex} = 365$ nm) and the values are reported by us earlier.^{30(a)} Due to lack of emission we cannot provide the quantum yields of pristine DPQ.

and wavelength in nm. In the present study $J_{Forster}$ values for F10C-PTZ in four different solvents were calculated by "PhotochemCAD" software⁴⁹ and the data were summarized in Table 5. The spectral overlap term ($J_{Forster}$) calculated vales are 1-7.6 x 10⁻¹⁴ cm⁶ mmol⁻¹, and the Forster rate of energy transfer ($k_{Forster}$) values are in the range of 12 – 27 x 10¹¹ s⁻¹ in F10C-PTZ dyad. Similar to our results, the efficient singlet-singlet energy transfer via Forster mechanism was observed in corrole-Imide dyads.^{21(c)}

Table 5. Energy transfer data of F10C-PTZ dyad in all the investigated solvents $\!\!\!^{\rm a}$.

Solvent	%Q	%T _(obs)	K _{obs} (10 ⁹ s ⁻¹)	^b J _{forster} (ст ⁶ ттоГ ¹) ^с	^b k _{Forster} (10 ¹¹ s ⁻¹)
PhMe (η =1.496 ε =2.38) ^d	99.9 ,	89	61.2	7.6509 X 10-14	12.062
CH2Cl2 (η =1.424 ε =8.93) ^d	99.9 ,	85	58.9	1.0258X 10-13	27.433
MeCN (η =1.344 ε =37.5) ^d	99.0 ,	79	56.25	2.0345X 10-14	15.682
DMF (η=1.43, ε=36.7) ^d	98.9	75	49.17	2.8848 X 10-14	13.866

^aError limits: %Q, K_{obs} ±8, %T_{(obs}) ± 15%, ^bK² = 0.66 in all the cases, and R_{c-c} = 8.30 Å (F10C-PTZ). ^cSpectral overlap term calculated from photochemCAD software. ^d η and ϵ refer to refractive index and dielectric constant of the solvents, energy transfer efficiency (%T_{(obs})) was calculated from overlap of the excitation and absorption spectra. Spectra related to Quenching Efficiency (%Q) and Energy transfer efficiency (%T) of F10C-PTZ in toluene and DMF were shown in (Supporting information, Fig. S18) along with the free energy change (Δ Gen) in different solvents.

3.5.2. Selective excitation of corrole: Photoinduced electron

transfer from DPQ to corrole: When selectively excite the both dyads at 420 nm, where the corrole absorbs predominantly, the emission corresponding to corrole part of the dyad was quenched in both dyads in CH_2Cl_2 (Fig.4 (b)). By careful watching of Fig 2 and 4 it is obvious that the emission of corrole does not overlap, either PTZ or DPQ absorption, thus the corrole emission quenching cannot be ascribed to the energy transfer from excited state of corrole to

PTZ/DPQ, apart from other radiative and non-radiative deactivation processes, the main alternate process for quenching of the excited states, is the intramolecular photoinduced electron transfer (PET) from ground state of DPQ/PTZ to excited state of corrole. The PET can occur in D-A systems, either excitation of the D or the A, would leads to charge transfer state.⁴⁸ The free energy change for the reductive electron transfer, when selective excitation of corrole unit (λ_{ex} = 420 nm) in F10C-DPQ can be calculated by Rehm- Weller approach ⁵⁰ eq. (5).

$\Delta G (DPQ \rightarrow {}^{1}cor) = E_{CT} [(E^{ox}(DPQ) - E^{red}(cor)] - E_{0-0}(cor)$ (5)

Thermal free energy (ΔG) for charge separation of F10C-DPQ was found to be - 0.86 eV, the negative value of free energy clearly suggesting that possibility of the electron transfer from DPQ to corrole. Moreover the effective quenching of fluorescence emission of corrole part of the dyad (98%) in polar solvents than nonpolar solvents (50%) providing additional evidence for the electron transfer, the emission spectra of the dyad (λ_{ex} = 420 nm) in different solvents were shown in (Supporting information, Fig. S19) the more acceleration of electron transfer in polar solvents than the non-

polar solvents also consistent with the earlier reports. $^{\rm 48,\ 23(c)}$ In contrast to this, when excite the corrole unit (λ_{ex} = 420 nm) in F10C-PTZ, very less quenching (45%) was observed when compare to fluorescence of pristine corrole intensity, although the quenched emission does not fallow the solvent trend (Fig. S18). it is important to mention that, the fluorescence emission quenching due to singlet-singlet energy transfer may or may not depends on the solvent polarity but the fluorescence emission quenching due to photoinduced electron transfer must depends on solvent polarity (vide infra). Moreover, in case of F10C-PTZ the thermal free energy for charge separation is ($\Delta G = -0.56 \text{ eV}$). In spite of the higher free energy, there was no charge transfer was observed in F10C-PTZ dyad, this might be dug_1 to, the free energy probably insufficient to separate the charges. From the electrochemical data (Table-1), these was no shift in the redox potentials of the F10C-PTZ dyad when compare to monomeric entities (PTZ/corrole), also providing additional evidence for the lack of charge transfer. The comparison of emission intensity of dyads with respect to their monomers I(dyad) / I(ref) in equi-absorbing solutions when excited at 420 nm

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have shown in (Supporting info. Table S2), from the data, it is observed that, in case of F10C-DPQ dyad, the emission was quenched effectively with respect to its monomer corrole and fallowed solvent trend. Whereas, in case of F10C-PTZ dyad, less extent of quenched emission was observed, moreover the quenched emission does not fallowed solvent trend. All these results corroborate, the decrease in fluorescence intensity cannot be attributed to electron transfer in F10C-PTZ dyad. Hence this decrease may be due to excited state and ground state interactions between the two chromophores units in the dyad, leading to lower the quantum yields.⁴⁸

3.6. Time resolved emission spectra

Additional information with regards to the fate of the excited states was obtained from time-resolved fluorescence studies carried out by the Time-correlated single photon counting (TCSPC) method. An improvement in time resolution to picoseconds was achieved by using picosecond laser pulses and MCP-PMT detection. Earlier we have reported the lifetime of pristine PTZ (λ_{ex} = 310 nm) in various solvents. The decay curves of pristine corrole (tpfc) shown in (Supporting information, Fig. S20) and the decay parameters collected in Table 6, the life time data of monomer corrole is well

agreement with the previous reports.^{21 (b)} Apart from this we cannot provide lifetime of pristine DPQ due to non-emissive nature. In addition to this, when we record PTZ lifetime in F10C-PTZ dyad (λ_{ex} = 310 nm), we could not fit the data due to infant emission, which is consistent with the study-state emission data. The

fluorescence decay of the dyads when excite at acceptor unit of the dyad (λ_{ex} = 420 nm), giving an additional support for photoinduced electron transfer. The decay parameters of the dyads investigated in four different solvents were shown in Fig. 6 and the data were summarized in Table 6.



Fig. 6. Fluorescence decays of dyads (a) F10C-PTZ, (b) F10C-DPQ at 420 nm. All the decay curves were monitored at their respective emission wavelengths according to Table 4.

From Table 6 data, and Fig. 6. It is observed that, in case of F10C-PTZ the decay curves are fitted with single-exponential decay with the lifetimes are in nanosecond (ns) region and there is no much difference when compare to lifetimes of the pristine corrole in all the investigated solvents, indicating the absence of photoinduced processes (PEnT/ PET).

Table 6. Fluorescence decay parameters of dyads along with their monomers.^a

		τ, (ps)			
Compound	λ_{ex} , nm	CH ₂ Cl ₂	PhMe	MeCN	DMF
tpfc	420 ^b	3872	3655	3503	3155
F10C-PTZ	420 ^b	1890	2811	2723	2610
F10C-DPQ	420 ^b	1980	1975	172	168

 a All lifetimes are in picoseconds (ps), error limits of τ $\,$ 10%. Relative

amplitudes are close to 100% of corresponding decay component. Emission monitored at corresponding emission wavelength in different solvents according to their respective emission values.

Furthermore we did not observe any solvent dependence on the decays, clearly indicating that the absence of charge transfer in F10C-PTZ dyad, which is consistent with the study-state emission data. In contrast to this, in case of F10C-DPQ the decay curves are fitted with biexponential in polar solvents with picoseconds (ps) lifetime has maximum amplitude. The major component, with shorter lifetime is attributed to photoinduced electron transfer from ground state of DPQ to excited state of corrole. Whereas, the other longer lifetime component with very less amplitude, may be the unquenched or no suitable orientation of the dyad which does not participate in electron transfer. The rate constant for the PET from DPQ to corrole in F10C-DPQ is calculated by eq. (6).

$$k_{ET} = 1/\tau_{(dyad)} - 1/\tau_{(cor)}$$
 (6)

Where $\tau_{(dyad)}$ is lifetime of the dyad and $\tau_{(cor)}$ is the pristine corrole lifetime, the rates of electron transfer in various solvents as fallows, in toluene (2.31x10⁹s⁻¹), dichloromethane (2.46x10⁹s⁻¹), aceonitrile (5.49x10¹⁰s⁻¹) and dimethylformamide (5.66x10¹⁰s⁻¹). From these values the rate of electron transfer (k_{ET}) increased with increasing polarity of the solvent (PhMe < CH2CL2 < MeCN < DMF), clearly indicating the participation of electron transfer is the main reason for the excited state deactivation of corrole in the F10C-DPQ dyad. In order clear understanding the photophysical events in the both the dyads, we have constructed energy level diagram (Supporting information, Fig. S21) in which the energy of different levels was calculated from the redox and emission data.

4. Materials and methods

Materials

All chemicals were used as received unless otherwise noted. Spectroscopic grade solvents dichloromethane (CH_2Cl_2), dimethylformamide (DMF), Acetonitrile (MeCN), and Toluene (PhMe) were used to measure absorption, emission and

electrochemical properties. Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} (pre-coated aluminum sheets) from Merck. Column chromatography was performed on silica (200-400 mesh). In all cases dual solvent system was used and the major band was collected. All the reactions were carried out under nitrogen or argon atmosphere using degassed solvents and the apparatus was shielded from ambient light.

Instrumentation

¹H-NMR spectra were recorded on Avance-400 MHz and Bruker 600 MHz spectrometers in CDCl3 and TMS as an internal standard. ESI-MS spectra were recorded on an Esquire HCT PLUS. Study-state absorption and emission spectra of the samples were measured using a PerkinElmer Lambda 850 UVeVisible Spectrophotometer and Perkin Elmer LS55 luminescence Spectrophotometer (PE Company, USA) respectively. Fluorescence spectra were recorded at 25°C in a 1 cm quartz fluorescence cuvette. The cyclic voltammograms (CV) were performed using CHI-660E electrochemical analyzer. The electrochemical experiments were performed on 1 mM sample solution in dichloromethane solvent using 0.1 M tetrabutyl ammonium hexafluorophosphate (TBAPF6) as supporting electrolyte. The working electrode is glassy carbon, (Ag/AgCl) is the reference electrode and plantinum wire is an auxillary electrode. The time-resolved fluorescence decays were measured by using time-resolved fluorescence spectroscopic technology, and was detected by using a Renishaw confocal imaging spectrometer system (inViaReflex, UK). The excitation source was a Ti-sapphire laser (tuning range of 690-1040 nm, Mai Tai, Spectra-Physics, USA), which generates pulse widths of approximately 100 fs at a repetition rate of 80 MHz and a pulse energy of 2 nJ. The fluorescence was collected through the objective, separated from the excitation laser by a dichroic mirror, and detected with a MCP-PMT detector (SPC-150, HAM-R3809U-50, Hamamatsu, Japan) placed in the back port of the microscope.

5. Conclusions

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In conclusion, we have synthesized two bichromophoric systems by approaching the preparation of two separate units (desired aldehyde and DPM) followed by a final cyclization step. This strategy provided a stable-meso substituted corroles (F10C-PTZ and F10C-DPQ) with a reasonable yield. For the first time we have synthesized and well characterized the 2,3-di(2- pyridyl)quinoxaline(DPQ) ligand formylation (DPQ-CHO) and succeeded to append to the corrole core. This work presents the first example of tetrapyrrole bearing a DPQ at its meso position, also rigidly connected PTZ at meso-position of stable corrole core. Both the absorption and electrochemical properties of the dyads, indicating the negligible interactions between these hetero chromophores. Fluorescence emission of the F10C-PTZ dyad was completely quenched when excite the dyad at 310 nm, is attributed to efficient energy transfer from PTZ to corrole with a remarkable efficiency, close to 100%. Whereas photoinduced electron transfer from ground state of DPQ to excited state of corrole was observed when excite the F10C-DPQ dyad at 420 nm. The donor DPQ entity, owing to its facile oxidation, yielded higher exothermicity for the light-induced charge separation process. In contrast to F10C-DPQ, there are no significant changes in photophysical properties of F10C-PTZ when excited at 420 nm. A detailed study of the excited state deactivation of both the dyads differentiated them as one dyad mimic's primary process and other mimics reaction center events in photosynthesis. Finally the structural similarity of donor entities with herero atom (N or S)

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featured "acene"s, as well as the LUMO energy's are lower than the (-3.15 eV) in both the dyad, which indicating that the suitability of dyads for n-channel field effect transistors (OFETs) applications.⁵¹ The Proton triggered emission studies of F10C-DPQ dyad, OFETs studies and DNA photocleavage studies of these dyads are underway.

Conflicts of interest

The authors declare no competing financial interest.

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Graphical Abstract:



Singlet-singlet energy transfer and electron transfer processes in corrole-phenothiazine and corrole-DPQ dyads was demonstrated by using electrochemical and fluorescence (study-state and time-resolved) spectral studies.