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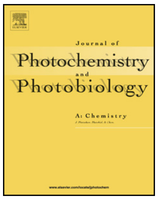

Intramolecular photoinduced reactions in corrole–pyrene and corrole–fluorene dyad systems

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ABSTRACT

We have designed and synthesized donor–acceptor conjugates in which donor polycyclic aromatic hydrocarbons such as either pyrene or fluorene linked at the pyrrole-β position of a corrole using vinylene spacer. Both the dyads are characterized by elemental analysis, MALDI-MS, ^{1}H NMR, UV–vis and fluorescence spectroscopy (steady-state and time-resolved) as well as electrochemical method. The Soret absorption band of corrole was split in both the dyads and more over both Soret and Q bands are red-shifted by 15–25 nm as compared to the unsubstituted corrole. Ground state properties indicate that there is a moderate π–π interactions in these dyad systems. However, fluorescence emission of polycyclic aromatic hydrocarbons of both the dyads quenched significantly (88–98%) compared to their monomeric units. The quenched emission was attributed in terms of intramolecular excitation energy transfer, which competes with the photoinduced electron transfer reaction in these dyads.

1. Introduction

The development of efficient light harvesting systems that mimic the natural photosynthetic process requires a fundamental understanding of the structural–functional relationship between various donor and acceptor chromophores [1–5]. During the photosynthesis, light energy is harvested in manifold types of antenna systems and funneled to "*special pair*" dimer of chlorophyll or bacteriochlorophyll molecules that initiate primary charge separation, ejecting an electron to become a dimer radical cation [6].

Several molecular and supramolecular dyads, triads, tetrads, etc. have been elegantly designed and studied with an emphasis on generating long-lived charge separated states through a charge migration route, and for the construction of systems that are capable of performing "*antenna reaction center*" events [7–11]. Owing to its resemblance to the natural photosynthetic chlorophyll pigment and relatively easy synthetic manipulations, porphyrin as the primary photoactive entity has dominated this area of research [12,13]. Additionally, several porphyrin-like molecules with interesting photo- and redox properties, *viz.*, phthalocyanines [14–16], naphthalocyanines [17], sub-phthalocyanines [18], chlorins [19,20], N-confusedporphyrins [21], fused porphyrins [22,23], hetero porphyrins [24], and expanded porphyrins [25] have also been successfully utilized in the construction of donor–acceptor systems.

Corroles are aromatic tetrapyrrolic macrocycles containing one carbon atom less compared to porphyrins and relatively unexplored area until recently. However, after the discovery of easy synthetic routes for *meso*-substituted corroles by Gross et al. and Paolesse et al. in 1999, investigations of corroles have been increased significantly [26,27]. When compared with porphyrins, corroles are tribasic aromatic macrocycles exhibit interesting properties which include lower oxidation potentials, higher fluorescence quantum yields, larger Stokes shift, and relatively more intense absorption of red light [28–30]. A few donor (D)–acceptor (A) systems based on corroles have been reported in the literature to understand natural photosynthetic phenomena [31–35]. For example, Flamigni and Gryko et al. have reported a multichromophoric array in which corrole (C) as central unit to perylenebisimide (PI) and N-[4-(phenylethynyl)phenyl]-N,N-diphenylamine (TPA) at the – *meso* positions of corrole [32]. Photophysical measurements showed efficient energy transfer to occur from the diphenyl acetylene substituted aromatic amine (99%) and perylenebisimide unit (100%) to the corrole and subsequent electron transfer from the corrole to perylenebisimide (97% efficient) with charge separated state lifetime of 1.9 ns and identified as TPA-C$^+$-PI$^-$. D'Souza and co-workers have used – *meso* positions of donor corrole and constructed corrole–fullerene dyads

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with rate of charge separated state ~10^{10}–10^{11} s^{-1} [33]. To the best of our knowledge corrole based D–A systems have been reported in literature by using – meso phenyl position/s not pyrrole-β position. It was well demonstrated in porphyrins that the rate of energy and electron transfer reactions were effected not only due to the spacer between D–A systems but also the place where it connected to porphyrin *i.e.*, either at – *meso* phenyl or pyrrole-β [36]. During the course of our research on excitational energy transfer (EET) and photoinduced electron transfer (PET) reactions of D–A systems on porphyrins and its closely related structures, we realized that the pyrrole-β position of corrole would be another effective site for making efficient conjugation in D–A systems. Here, in the present study we have linked energy/electron donor polycyclic aromatic hydrocarbon (**PAH**) systems such as either pyrene (**PYR**) or fluorene (**FLU**) at pyrrole-β position of corrole macrocycle. Both the D–A systems have been characterized by UV–vis, MALDI-MS, ^{1}H NMR spectroscopy and electrochemical methods. In addition, more emphasis has been given on photophysical properties of these D–A systems.

2. Experimental

2.1. Materials

Commercially available reagents and chemicals were procured from Sigma–Aldrich. A.R. grade solvents were used for synthesis. All solvents were distilled prior to the column chromatography. Dichloromethane and N,N-dimethyl formamide were dried in presence of calcium hydride under nitrogen atmosphere. ACME silica gel (100–200 mesh) was used for column chromatography. Thin-layer chromatography was performed on Merck-precoated silica gel 60-F254 plates. Either gravity or flash chromatography was performed for purification of all compounds. All the reactions were carried out under nitrogen or argon atmosphere using dry and degassed solvents in the absence of light.

2.2. Synthesis

5,10,15-Tritolyl corrole (**TTC**), 3-Formyl-5,10,15-tritolyl corrole (**TTC–CHO**) were synthesized according to the literature procedures [37,38].

2.2.1. 3-hydroxymethyl-5,10,15-tritolylcorrole (TTC-CH$_2$OH)

3-Formyl-5,10,15-tritolylcorrole **TTC–CHO** (1.8 g, 3.02 mmol) was dissolved in chloroform (250 ml) and a solution of sodium borohydride (1.8 g) in absolute ethanol (250 ml) was added. The mixture was stirred for 1 h protected from moisture. Water (20 ml) was then added and the stirring was continued for a further 1 h. The mixture was partitioned and extracted with chloroform (2× 100 ml), dried over anhydrous sodium sulfate and the solvent was removed under vacuum. The crude residue was subjected to flash silica gel column chromatography with chloroform-methanol mixture (98:2) as eluent. A dark blue-colored band was collected. After removing the solvent, a violet-colored solid was obtained as 3-hydroxy methyl-5,10,15-tritolylcorrole **TTC-CH$_2$OH** (1.75 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$, 28 °C): δ = 2.18 (s, 1H), 2.65 (s, 9H), 4.9 (s, 2H), 7.50 (m, 6H), 7.90–8.20 (m, 6H), 8.40–8.80 (m, 7H); ESI-MS: *m*/*z* 599; UV–vis (CH_2Cl_2): λ_{max}, (log ε) = 414 (5.15), 576 (4.32), 617 (4.22), 645 (4.10).

2.2.2. Triphenyl[[5,10,15-tritolylcorrole-3-yl]methyl]phosphoniumbromide (TTC-PPh$_3$·Br)

TTC-CH$_2$OH (600 mg, 1 mmol) and triphenyl phosphoniumhydrobromide **PPh$_3$·HBr** (375 mg, 1.1 mmol) was dissolved in 100 ml chloroform and refluxed for 2 h. Removal of the solvent and the mixture was subjected to the silica gel column chromatography using the chloroform and methanol mixture (9:1) as eluent. A dark green-colored band was collected and evaporation of the solvent afforded a purple solid **TTC-PPh$_3$·Br** (820 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$, 28 °C): δ = 2.65 (s, 9H), 5.45 (s, 2H), 6.90 (s, 5H), 7.02 (s, 1H), 7.15 (m, 6H), 7.30–760 (m, 11H), 7.80–8.50 (m, 10H), 8.70 (s, 1H); ESI-MS: *m*/*z* 844 (M^+–Br), 597 (M^+–PPh_3•Br); UV–vis (CH_2Cl_2): λ_{max}, (log ε) = 420 nm (5.05), 575 (4.08), 618 (4.09), 656 (4.15), 716 (4.05).

2.2.3. 5,10,15,-Tritolyl-3-(2-pyren-1-yl-vinyl)corrole (TTC-PYR)

Pyrene-2-aldehyde **PYR-CHO** (62 mg, 0.27 mmol), 18-crown-6 ether (8 mg) and anhydrous potassium carbonate (75 mg, 0.54 mmol) were dissolved in 20 ml of anhydrous DMF. Then, the DMF solution (20 ml) of **TTC-PPh$_3$·Br** (250 mg, 0.27 mmol) was slowly added to the above mixture under vigorous stirring at room temperature. The reaction was completed within 2 h. The reaction mixture was poured into water and filtered the dark-purple solids (a mixture of *E* and *Z*-isomers), which was then subjected to column chromatography in silica gel. The solvent was evaporated in vacuo and the resulting residue was dissolved in 30 ml THF followed by reflux in the presence of catalytic amount I_2 for 8 h. The mixture was poured into aqueous NaOH solution (0.5 N) to remove unreacted I_2. The organic layer was extracted with dichloromethane, dried over anhydrous sodium sulfate. Then, the solvent was removed and the resulting mixture was purified by silica gel column chromatography using dichloromethane-petroleum ether (8/2: v/v) as the eluent to give the *E*-isomer as purple solids, 90 mg, yield 41%. Anal. Calcd. for $C_{58}H_{42}N_4$% (794.98): C, 87.63; H, 5.33; N, 7.05. Found C, 87.67; H, 5.30; N, 7.01.^{1}H NMR (500 MHz, $CDCl_3$, 28 °C): δ = −1.45 (3H, brs), 2.65 (s, 9H), 7.50–7.60 (m, 10H), 7.95 (m, 3H), 8.08 (m, 6H), 8.27 (m, 2H), 8.40 (m, 3H), 8.55–8.65 (m, 4H), 9.02 (s, 1H), 9.80 (s, 1H); MALDI-MS: *m*/*z* 794 (M^+, 100%); UV–vis (CH_2Cl_2): λ_{max}, (log ε) = 279 (4.53), 348 (4.55), 442 (4.95), 463 (5.05), 613 (428), 644 (4.37), 673 (4.23).

2.2.4. 5,10,15,-Tritolyl-3-(2-fluorene-1-yl-vinyl)corrole (TTC-FLU)

Fluorene-2-aldehyde **FLU-CHO** (50 mg, 0.35 mmol), 18-crown-6 ether (10 mg) and anhydrous potassium carbonate (100 mg, 0.70 mmol) were taken in 20 ml of dry DMF. Then, the K_2CO_3 solution (20 ml) of **TTC-PPh$_3$·Br** (323 mg, 0.35 mmol) was slowly added to the above mixture under vigorous stirring at room temperature. Similar to the preparation of **TTC-PYR**, the reaction procedure and purification method was adopted to afford the corresponding *E*-isomer of **TTC-FLU** as purple solids, 105 mg, yield 39%. Anal. Calcd. for $C_{55}H_{42}N_4$% (758.94): C, 87.04; H, 5.58; N, 7.38. Found C, 87.00; H, 5.60; N, 7.35.^{1}H NMR (500 MHz, $CDCl_3$, 28 °C): δ = −1.38 (3H, brs), 2.65 (s, 9H), 3.85 (s, 2H), 7.35 (m, 2H), 7.50–7.80 (m, 12H), 7.95–8.20 (m, 6H), 8.40–9.0 (m, 8H); MALDI-MS: *m*/*z* 758 (M^+, 100%); UV–vis (CH_2Cl_2): λ_{max}, (log ε) = 226 (4.40), 308 (4.47), 341 (4.51), 431 (4.90), 454 (4.87), 606 (4.18), 639 (4.22), 671 (4.08).

2.3. Methods and Instrumentation

^{1}H NMR spectra were recorded on a 500 MHz INOVA spectrometer. MALDI-TOF MS analysis was performed with a Shimadzu Biotech AXIMA instrument equipped with a nitrogen laser in the linear mode using 2,2′:3′,2″-terthiophene as the matrix. Cyclic and differential pulse voltammetric measurements were performed on a PC-controlled electrochemical analyzer (CH instruments model CHI620C). All these experiments were performed with 1 mM concentration of compounds in dichloromethane at a scan rate of 100 mV s^{-1} in which tetrabutyl ammonium perchlorate (TBAP) is