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Ultrafast charge separation and charge stabilization in axially-linked ‘tetrathiafulvalene - aluminum(III) porphyrin - gold(III) porphyrin’ reaction center mimics†

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The axial bonding ability of aluminum(III) porphyrin (AlPor) has been exploited to synthesize vertically-linked dyad, ‘aluminum(III) porphyrin – gold(III) porphyrin’ (AlPor-Ph-AuPor^{+}), and the two corresponding self-assembled triads, ‘tetrathiafulvalene – aluminum(III) porphyrin – gold(III) porphyrin’ (TTF-py→AlPor-Ph-AuPor^{+} and TTF-Ph-py→AlPor-Ph-AuPor^{+}). The unique topology of these triads provides an excellent opportunity to investigate the sequential electron transfer in the perpendicular direction to AlPor plane where the AlPor acts as photosensitizer and primary electron donor while the AuPor and TTF serve as an electron acceptor and donor, respectively. Ground state properties of the dyad and triad suggest that there are no direct intramolecular interactions between the oppositely disposed AuPor and TTF units of the triad. However, the NMR and UV-visible absorption studies of the dyad reveal intermolecular interactions in non-coordinating solvents due to the coordination of counterion PF_6^- to the Al center of AlPor. Steady-state and femtosecond transient absorption studies of the dyad show that the lowest excited singlet state of AlPor (^{1}AlPor*) is strongly quenched by ultrafast electron transfer to AuPor^{+} with a time constant of 3.16 ps. The resulting charge separated state (AlPor$^{+\bullet}$-AuPor$^{\bullet}$) decays to ground state biexponentially with time constants of 27.26 and 2557 ps. Analogously, upon photo-excitation the triads also produce the same primary radical pair (AlPor$^{+\bullet}$-AuPor$^{\bullet}$). However, the formed radical pair is further involved in a rapid hole transfer from AlPor$^{+\bullet}$ to TTF to form a stable final radical pair TTF$^{+\bullet}$-AlPor-AuPor$^{\bullet}$. Lifetime of the charge separated state exhibits an increase from 27.26 ps in AlPor-Ph-AuPor to 1393 ps in TTF-py→AlPor-Ph-AuPor^{+} and 1484 ps in TTF-Ph-py→AlPor-Ph-AuPor^{+}. These results reveal successful charge stabilization in the self-assembled supramolecular reaction center mimics constructed via axial linkage strategy.

1. Introduction

Photosynthesis is nature’s most well-designed process, in which sunlight is converted into chemical energy.[1, 2] In this process, the fundamental reactions such as photoinduced energy transfer (EnT) and electron transfer (ET) between photosynthetic molecular components are well optimized to drive the desired reactions towards conversion of solar energy into chemical energy. Over the last few decades, a significant amount of progress has been achieved in terms of understanding the factors that govern EnT and ET in photosynthesis by using multi-component synthetic models with the objective of tapping the solar energy for future energy needs.[3-17] Within these synthetic models, porphyrin (Por) molecules have emerged as promising building blocks for construction of multi-component donor-Por-acceptor systems where they mimic the role of chlorophyll pigment of natural photosynthesis. This is because porphyrins are easy to functionalize, absorb strongly in the visible region, are often highly fluorescent, have rich redox chemistry, and moreover their optical and redox properties are easily tunable.[18] However, most of these model compounds are based on the transition metal porphyrins. Moreover, their photoinduced processes are focused along the plane of the porphyrin. Very few examples are known where the photoinduced processes are in axial or perpendicular direction to the porphyrin plane.[19-25] This is mainly because of the synthetic challenges where two ligands cannot be attached using transition metal porphyrins. This problem can be addressed by using main group element porphyrins, such as aluminum(III) porphyrin,[26-29] tin(IV) porphyrin[27, 30-36] or phosphorus(V) porphyrins,[27, 30, 37-40] which generally have one or two axial bonds and they can be utilized to attach redox active electron donor (D) and/or acceptor (A) units.

Among the main group porphyrins, aluminum(III)porphyrins (AlPor) are unique, because the axial hydroxide of AlPor reacts with carboxylic acids to form covalent ester linkages while Lewis bases such as pyridine and imidazole form coordination bonds to the Al centre, which is a

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† Electronic Supplementary Information (ESI) available: [Synthesis details, NMR and absorption spectra, titrations (absorption and florescence), spectral overlap and transient absorption spectra]. See DOI: 10.1039/x0xx00000x

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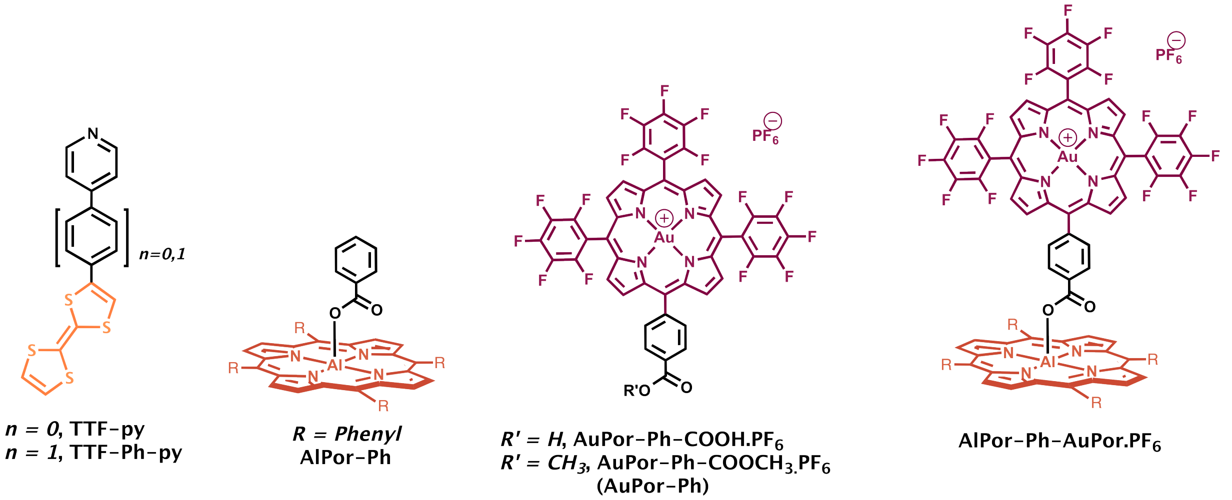

Chart 1. Structural information of investigated compounds in this study.

Lewis acid.[41-46] The combination of these properties makes AlPor a unique candidate for constructing 'axial-bonding' type multi-component D-AlPor-A systems. Over the last few years, we have reported a few novel AlPor based D-AlPor-A systems consisting of three-dimensional (3D) fullerene or two-dimensional (2D) naphthalenediimide as an electron acceptor; and ferrocene, tetrathiafulvalene or phenothiazine entities as secondary electron donors.[47-51] In these systems, the EnT and ET reactions were investigated in the axial direction as a function of electronic coupling, orientation, reorganization energy, and the distance between donor and acceptor units. More recently, we reported AlPor based dyad (AlPor-Ph-H_2Por) where axially bound fluoro-substituted free-base porphyrin (H_2Por) was projected as a two-dimensional (2D) electron acceptor to study the electron transfer in axial direction.[52] However, due to the strong spectral overlap between AlPor emission and H_2Por absorption, it was found that the H_2Por unit acts as an energy acceptor rather than electron acceptor. By altering the optical and redox properties of axial H_2Por unit it is possible to change its role in photoinduced processes. One-way to tune the optical and redox properties of axial H_2Por unit is metalation.

In the present study we have chosen gold(III) as a metal ion because its insertion (that is formation of $AuPor^+$) results in: (i) decrease in spectral overlap between AlPor emission and $AuPor^+$ absorption, (ii) positive shift in redox potentials, and (iii) increase in the first excited singlet state of acceptor porphyrin ($AuPor^+$). Together with these alterations, electron transfer is expected to outcompete the singlet-singlet energy transfer from AlPor to $AuPor^+$ in newly synthesized dyad AlPor-Ph-$AuPor^+$ (see Chart 1) and thus guarantee the sequential electron transfer in its corresponding triads (TTF-py→AlPor-Ph-$AuPor^+$ and TTF-Ph-py→AlPor-Ph-$AuPor^+$, see Fig. 1) where the electron transfer could be studied in axial direction as a function of distance. On the other hand, gold(III) porphyrins are often used as electron acceptors in D-A systems.[53-55] Due to the heavy atom effect of gold metal, its first excited singlet state undergoes rapid intersystem crossing to form a triplet state.[56] The formed triplet state can undergo electron transfer and it can be involved in triplet–triplet energy transfer processes.[57, 58] Hence, gold(III) porphyrin as an electron acceptor in the present study will enable us to study the participation of its triplet state in photoinduced processes. We have chosen tetrathiafulvalene (TTF) as the secondary donor because of its strong electron donating ability, which makes it an excellent candidate as a reductive electron quencher or hole acceptor in D-A systems.[24, 37, 59-61] The general structures of the dyad and its corresponding triads are shown in Chart 1 and Fig. 1, where the TTF and fluoro-substituted gold(III) porphyrin ($AuPor^+$) units are located on opposite faces of the AlPor. We will show that efficient ultrafast electron transfer occurs between AlPor and $AuPor^+$ in the dyad as well as triads. Furthermore, formed primary charge separated state is stabilized by charge shift from TTF unit in the case of triads.

2. Experimental section

2.1 Synthesis

All chemicals and solvents used in this study were purchased from either Sigma-Aldrich Chemical Co. or Alfa-Asear. The

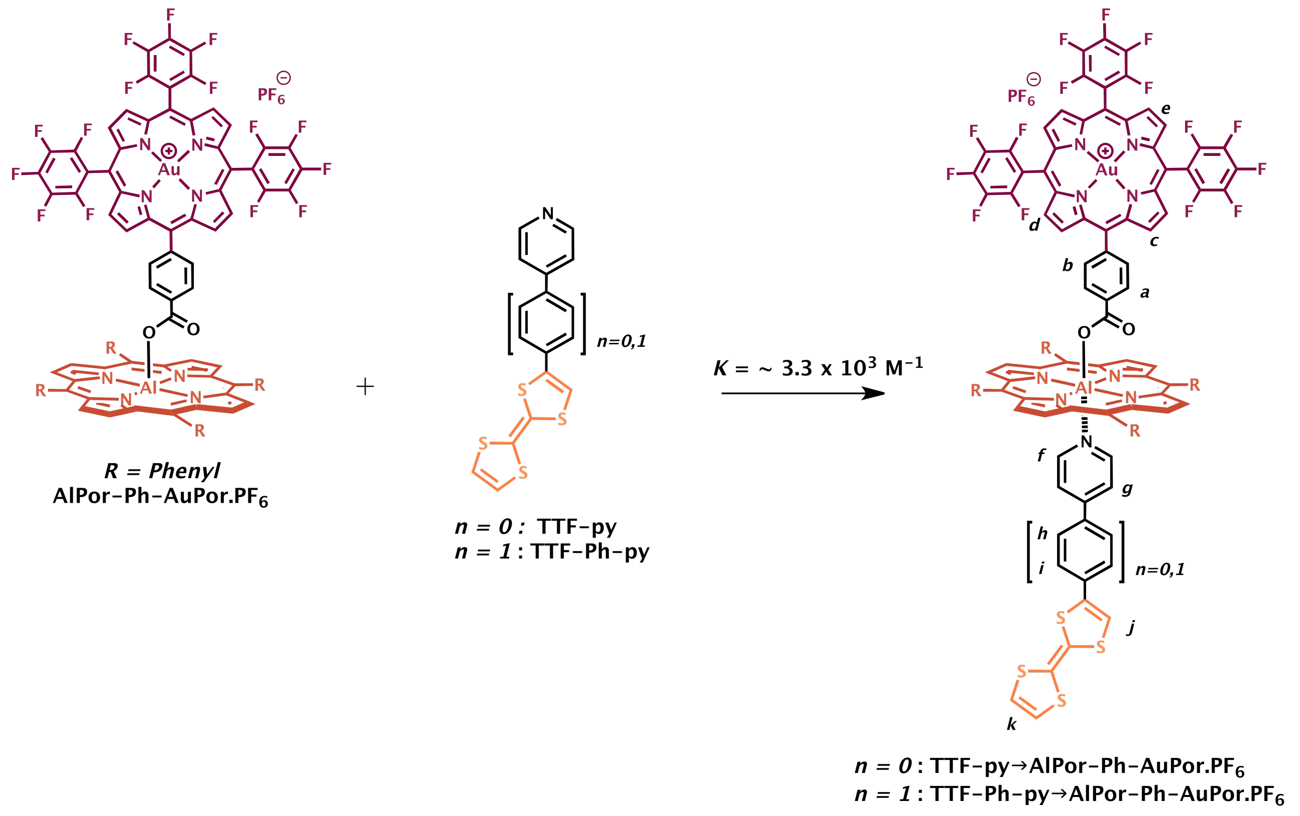

Fig. 1 Formation of vertically arranged self-assembled supramolecular triads through Lewis acid-base interactions.

synthesis of 5,10,15,20-tetra(phenyl)-porphyrinatoaluminum(III)hydroxide (AlPor-OH) and the reference compound AlPor-Ph have been previously reported.[48] The pyridine appended tetrathiafulvalene derivatives (TTF-py and TTF-Ph-py) and precursor porphyrins (5-(4-methylcarboxyphenyl)-10,15,20-tri(pentafluorophenyl) porphyrin (H_2Por-Ph-$COOCH_3$, from now on referred to as H_2Por-Ph), 5-(4-carboxyphenyl)-10,15,20-tri(pentafluorophenyl)porphyrin (H_2Por-Ph-COOH)) have been reported elsewhere, Scheme S1.[50] Gold(III) porphyrin derivatives, 5-(4-methylcarboxyphenyl)-10,15,20-tri(pentafluorophenyl)porphyrinatogold(III) hexafluorophosphate (AuPor-Ph-$COOCH_3$.PF_6, from now on referred to as AuPor-Ph.PF_6) and 5-(4-carboxyphenyl)-10,15,20-tri(pentafluorophenyl)porphyrinatogold(III) hexafluorophosphate (AuPor-Ph-COOH.PF_6), were prepared according to the reported methods,[62] see supplementary information for details.

2.2 Preparation of AlPor-Ph-AuPor.PF_6.

AlPor-OH (10 mg, 0.015 mmol) and AuPor-Ph-COOH.PF_6 (20 mg, 0.016 mmol) were dissolved in 10 mL of dry dichloromethane. The resulting solution was sonicated for 5 min and then stirred for 12 h at room temperature under nitrogen atmosphere. The solvent was removed under reduced pressure and washed with hexane to get the pure dyad as a purple solid. Yield: 27 mg (93%). Mass (ESI): m/z 1761.2504 $[M-PF_6]^+$, calculated 1761.2516 for $C_{89}H_{40}AlAuF_{15}O_2N_8$. ^1H NMR (300 MHz, CD_3CN) ppm: 9.64 (s, 8H), 9.41 (bs, 2H), 9.04 (m, 10H), 8.29 (bs, 8H), 7.79 (m, 12H), 7.34 (bs, 2H), 5.01 (d, 2H, J = 9.0 Hz). ^1H NMR ($CDCl_3$, 300 MHz) ppm: 9.42 (bs, 4H), 9.10 (m, 10H), 8.82 (bs, 2H), 8.25 (m, 8H), 7.75 (m, 12H), 7.26 (bs, 2H), 5.60 (bs, 2H). ^{31}P NMR ($CDCl_3$, 121 MHz) ppm: −143.33.

3. Physical methods

3.1 NMR Spectroscopy and Mass Spectrometry

^1H NMR, ^1H-^1H COSY and ^{31}P NMR spectra were recorded with Bruker Avance 300 MHz NMR spectrometer using $CDCl_3$ or CD_3CN as the solvent. High resolution mass spectrometry analysis was performed on an LTQ Orbitrap Velos mass spectrometer (ThermoScientific) using an ESI ion source operating in positive mode with a resolution of 30,000, monitoring a mass range from 150-2000 atomic mass units (amu).

3.2 Voltammetry

Cyclic voltammetric experiments (dichloromethane, 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$)) were performed on the Potentiostat/Galvanostat Model 283 (EG & G Instruments, Princeton Applied Research) electrochemical analyser (working electrode: platinum, auxiliary electrodes: Pt wire; reference electrode: Ag/AgCl). The Fc^+/Fc (Fc = ferrocene, $E_{1/2}(Fc^+/Fc)$ = 0.48 V *vs* SCE in CH_2Cl_2, 0.1 M $TBAClO_4$ under our experimental conditions) redox couple was used to calibrate the potentials, which were reported in V *vs* SCE. Spectroelectrochemical study was performed by using a cell assembly (SEC-C) supplied by ALS Co., Ltd. (Tokyo, Japan). This assembly comprised of a Pt counter electrode, a 6 mm Pt Gauze working electrode, and an Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The optical transmission was limited to 6 mm covering the Pt Gauze working electrode.

3.3 Steady-state UV-visible absorption and emission spectroscopy

The UV-visible spectra were recorded with a Varian Cary 50 Bio UV-VIS spectrometer. Concentration of the samples used for these measurements ranged from 1×10^{-6} M (porphyrin Soret band) to 5×10^{-5} M (Q-bands) solutions. Steady-state fluorescence spectra were recorded using a Photon Technologies International LS-100 luminescence spectrometer (L-format), equipped with a 70 W xenon lamp, running with Felix software. The low temperature (77K) spectra were collected using a home build spectrofluorimeter equipped with Triax 320 spectrograph and Jobin Yvon Symphony CCD detector. The emission (fluorescence and phosphorescence) data were collected using optically matched solutions, hence the emission intensities are directly comparable.

3.4 Absorption and fluorescence titrations

Absorption titrations were carried out in dry dichloromethane at concentration of 6×10^{-5} M appropriate for measuring the porphyrin Q bands. A solution containing the acceptor (A = $AlPor\text{-}Ph\text{-}AuPor^+$ or AlPor-Ph) was placed in a cuvette and titrated by adding aliquots of a concentrated solution of the donor (D = TTF-py, TTF-Ph-py or py). The donor solution also contained the acceptor at its initial concentration so that the porphyrin concentration remained constant throughout the titration. The binding constants were calculated using the Benesi-Hildebrand equation,[63] $[A]/Abs = (1/[D])(1/\varepsilon K) + (1/\varepsilon)$, where, [A] is the total concentration of bound and unbound acceptor and is kept fixed, Abs is the absorption of complex at the wavelength λ, [D] is the total concentration of the donor which is varied, K is binding constant and ε is the molar absorptivity of D-A complex. In an analogous manner, steady-state fluorescence titrations were carried out in dichloromethane using solutions at constant concentration of A and varying concentration of D. The solutions were excited at the isosbestic point wavelength, which was obtained from the corresponding absorption titrations.

3.5 Femtosecond laser flash photolysis

Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator, both provided by Ultrafast Systems LLC, was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into harmonic generator that produces second and third harmonics of 400 and 267 nm besides the fundamental 800 nm for excitation, while the rest of the output was used for generation of white light continuum. In the present study, the second harmonic 400 nm excitation pump was used in all the experiments. The absorbance of AlPor and AuPor are in ~1:5 ratio at this excitation wavelength. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

4. Results and discussion

4.1 Synthesis

Gold(III) metalation was performed by using $AuCl_3$ according to the reported methods.[62] However, low yields (20-25%) were obtained in our experimental conditions. Despite many other decent methods for gold metalation reported in the literature, we used this route due to limitations of our chemical inventory. The counter ion exchange was performed by dissolving the chloride salt in methanol and then precipitating as PF_6 salt by addition of saturated aqueous NH_4PF_6. The dyad, $AlPor\text{-}Ph\text{-}AuPor^+$, was prepared in quantitative yields (Scheme S2) by reacting equal molar ratios of AlPor-OH and $AuPor\text{-}Ph\text{-}COOH.PF_6$ in dichloromethane. Formation of the dyad was monitored by NMR spectroscopy. Obtained dyad was stored in a freshly prepared $CaCl_2$ desiccator prior to optical studies. The triads shown in Fig. 1 were assembled by using the dyad ($AlPor\text{-}Ph\text{-}AuPor^+$) and TTF-py/TTF-Ph-py derivatives in non-coordinating solvents. Lewis acid-base interactions were utilized to build these vertically arranged supramolecular self-assembled triads. NMR, UV-visible absorption and steady-state fluorescence titrations were employed to monitor the formation of triads. However, the formed self-assembled triads could not be isolated.

4.2 Structural Characterization

The mass spectrum of dyad AlPor-Ph-AuPor.PF_6 showed peaks at 1761 and 639 ascribable to the mass (m/z) of $[M{-}PF_6]^+$ and $[M{-}PF_6{-}\text{axial Por}]^+$, respectively. The ^1H NMR spectra of the dyad (AlPor-Ph-AuPor$^+$) and its axial unbound component (AuPor$^+$-Ph-COOH) were measured in $CDCl_3$ and are shown in Fig. S5 (top spectrum) and Fig. S3, respectively. As expected, shielding effects are observed for the proton of axial AuPor$^+$. Protons *a* and *b* that appear at 8.55 and 8.25 ppm in free AuPor$^+$-Ph-COOH compound are shifted to 5.60 and 7.26 ppm, respectively due to the ring current effect of the porphyrin macrocycle. Similarly, resonances due to the *β*-protons (*c*, *d* and *e*) are also shifted upfield compared to the corresponding resonances in the spectrum of compound AuPor$^+$-Ph-COOH. These chemical shifts (δ) agree well with those of axial bonding type porphyrin systems.[47-50, 52] However, the observed peaks are very broad and were found to be sensitive towards the concentration of the dyad, see Fig. S5. Interestingly, at higher concentration (Fig. S5, bottom spectrum) an additional peak at 5.11 ppm was observed for protons *a* suggesting that in some portion of the sample, the Al centre of AlPor exists in the hexavalent state. In a typical pentavalent AlPor, the Al centre lies out of the porphyrin plane and is pulled into the plane when it converts to the hexavalent complex due to the axial coordination.[47, 49, 50] If such a phenomenon exists in the dyad solution, the axial AuPor$^+$ could be brought even closer to AlPor ring, which may cause an additional shielding on protons *a* and therefore lower chemical shift. Since the spectrum is measured in non-coordinating solvent ($CDCl_3$), the possibility of the axial coordination by solvent can be safely ruled out. However, careful examination of the dyad structure reveals that the valency conversion is feasible if the counter ion PF_6^- from the dyad molecule is involved in such coordination, Fig. 2. The strong electron withdrawing nature of AuPor$^+$ (which will be discussed in the electrochemistry section) enhances the Lewis acidity of the Al center that can readily coordinate to a fluorine atom of PF_6^- ion, which typically acts as a strong Lewis base. Such behaviour has been noticed previously in other systems.[64] This type of Lewis acid-base interaction brings the dyad molecules closer to each other in solution and perhaps forms molecular aggregates. Moreover, this probability would be greater at higher concentrations. Fig. 2 shows the proposed hexavalent complex and it clearly explains the observed broad peaks and additional chemical shift for protons *a* at higher concentrations in a non-coordinating solvent. In contrast, coordinating solvents (e.g. CD_3CN) resulted in a well-resolved spectrum because the solvent is present in large excess and its coordination outcompetes the PF_6^- coordination with Al centre. Consequently, dyad molecules are expected to lie far from each other in solution. Therefore a well-resolved spectrum is observed, Fig. S6. Additionally, the Al centre is continually present in the hexavalent state, hence only one peak is observed for the protons *a* (at 5.00 ppm). The chemical shift of the ^{31}P NMR signal due to the counter ion phosphorus atom in the dyad appears at –143.38 ppm. Overall, the upfield shift of axially linked porphyrin confirms the structure of the investigated dyad molecule.

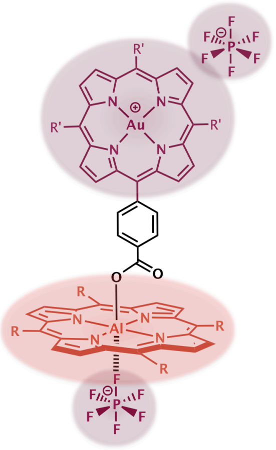

Fig. 2 The proposed hexavalent complex between the PF_6^- ion and the Al center of AlPor in non-coordinating solvents.

As shown in Fig. 1, the self-assembled supramolecular triads have been assembled from the components AlPor-Ph-AuPor$^+$ and TTF-py (or TTF-Ph-py). The NMR, UV-visible absorption and fluorescence spectroscopic methods were used to monitor the formation of triads. Fig. S7 shows the ^1H NMR spectrum of a 1:1 mixture of AlPor-Ph-AuPor$^+$ and TTF-py. In the coordination complex, shielding due to the porphyrin ring causes an upfield shift of TTF-py protons. The protons *f*, *g*, *j* and *k* appear at 8.61, 7.26, 6.85 and 6.37 ppm in free TTF-py, whereas in the triad they appear at 6.57, 6.63, 6.57 and 6.29 ppm. The magnitude of the shift depends on the distance of the protons from the porphyrin ring, and the pyridinyl protons (*f* and *g*) display the greatest shift indicating that coordination occurs via the pyridinyl group. On the benzoate bridging group to the AuPor$^+$, the protons *a* closest to the porphyrin ring show an increased upfield shift upon coordination. Overall, the observed changes in chemical shift suggest the formation of self-assembled triad TTF-py→AlPor-Ph-AuPor$^+$. Analogous results were obtained from the triad TTF-Ph-py→AlPor-Ph-AuPor$^+$ (Fig. S8).

4.3 UV-visible absorption spectroscopy

The UV-visible spectra of dyad AlPor-Ph-AuPor$^+$ and corresponding reference compounds (AlPor-Ph and AuPor$^+$-Ph) were measured in dichloromethane and are shown in Fig. 3a. The band positions (Q-bands and B- or Soret Bands) and their molar extinction coefficients are summarized in Table 1. The UV-visible absorption spectrum of the dyad reveals the absorption bands, which correspond to its reference porphyrins AlPor-Ph and AuPor$^+$-Ph. The majority of the absorbance at 406, 415, 520 and 550 nm is attributed to the AuPor$^+$ (75%), AlPor (90%), AuPor$^+$ (76%) and AlPor (80%), respectively. The molar extinction coefficients (ε) at 415 and 550 nm, which correspond to AlPor unit, are slightly lower than that of the reference AlPor-Ph compound. Moreover, the spectrum exhibited a new absorption band at 603 nm and was found to be sensitive to the concentration of the dyad as it appears only at higher concentrations, Fig. 3b. This behaviour is complementary with NMR results and supports the PF_6^- ion binding to the Al centre of AlPor to form the hexavalent AlPor,

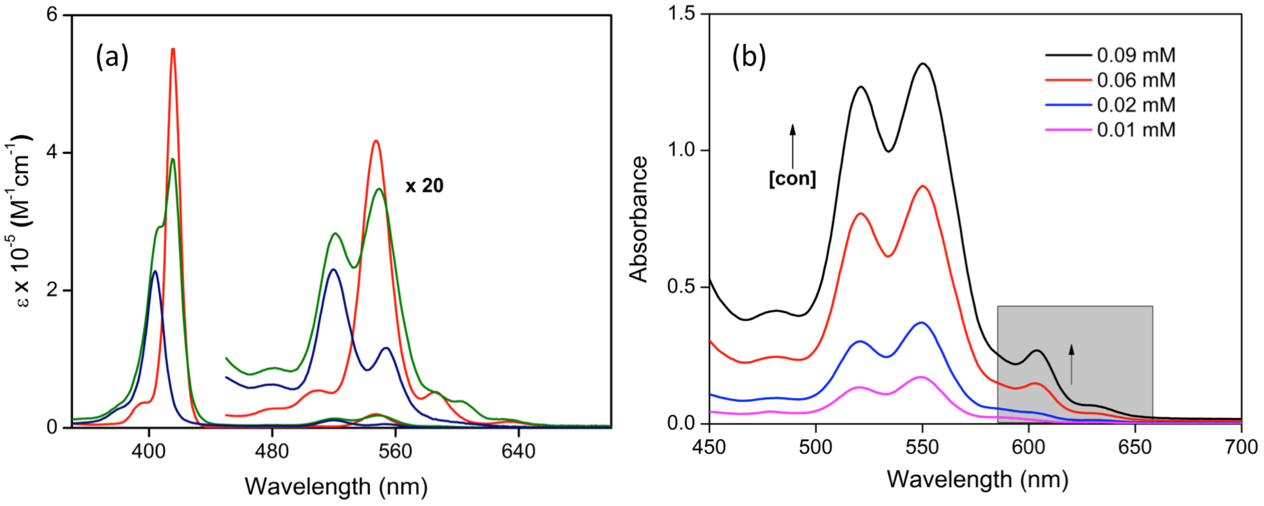

Fig. 3 UV-visible absorption spectra of (a) AlPor-Ph-AuPor$^+$ (green), AuPor$^+$-Ph (blue) and AlPor-Ph (red) in dichloromethane and (b) AlPor-Ph-AuPor.PF$_6$ in dichloromethane at different concentrations.

Fig. 2. The observed new band at 603 nm for AlPor-Ph-AuPor$^+$ is a characteristic feature of hexavalent AlPor.[47, 49, 50] Additionally, the lower ε values for bands at 415 and 550 nm are also a typical behaviour of hexavalent AlPor as these bands diminish during the conversion of pentavalent to hexavalent Al center.[47, 49, 50] The py-appended TTF derivatives (TTF-py and TTF-Ph-py) have relatively weak and very broad absorption bands at λ = 304 (average of 285 and 324 nm bands) and λ = 435 nm for TTF-py, and at λ = 298 and 428 nm for TTF-Ph-py, Fig. S9.[52] Overall, the absorption studies suggest that there are no interactions between basal (AlPor) and axial porphyrin (H_2Por or AuPor$^+$) units. Furthermore, the absorption bands of AlPor and AuPor are overlapping; therefore by choosing the wavelengths of 550/560 nm and 520 nm it is possible to excite mostly AlPor and the axial AuPor$^+$ units, respectively.

Fig. 4a shows the absorption titrations of TTF-py vs AlPor-Ph-AuPor$^+$ in dichloromethane. Upon addition of the TTF-py, the Q band at 549 nm of AlPor is shifted to 560 nm as well as the absorbance at 604 nm increases. Isosbestic point is observed at 555 nm, indicating the formation of triad TTF-py→AlPor-Ph-AuPor$^+$ in equilibrium, and the changes in the porphyrin bands are typical of axial coordination of nitrogen ligands to AlPor.[47, 49, 50, 52] Benesi-Hildebrandt analysis (Fig. 4a, inset) gives a linear plot indicating that a 1:1 complex is formed, and the slope yields a binding constant (K) ≈ 3.3 × 10^3 M^{-1}. In a similar fashion, the binding constant K was calculated

Table 1 UV-visible absorption, fluorescence and redox potential data of investigated compounds in dichloromethane.

Sample	Absorption λ_{max}, nm (log ε)		Fluorescence	Potential (vs SCE)[a]	
	B-Bands	Q-Bands/TTF	λ_{ex} = 550 nm λ_{em} (%Q)	Oxidation	Reduction
AlPor-Ph	416 (5.74)	585 (3.42), 547 (4.32), 510 (3.44)	595, 646	0.91	−1.21
AuPor$^+$-Ph	404 (5.36)	554 (3.77), 520 (4.06)	-	1.82	−0.28, −0.82
AlPor-Ph-AuPor$^+$	406 (5.46), 415 (5.59)	604 (3.28), 586 (3.41), 549 (4.24), 521 (4.15)	592, 644 (88%)	0.91, 1.16	−0.29, −0.82, −1.20
TTF-py	-	435 (3.45), 324 (4.17), 285 (4.22)	-	0.48, 0.83	-
TTF-Ph-py	-	428 (3.64), 298 (4.48)	-	0.47. 0.87	-

[a] Redox potential were measured in dichloromethane with 0.1 M TBAClO$_4$ as a supporting electrolyte.

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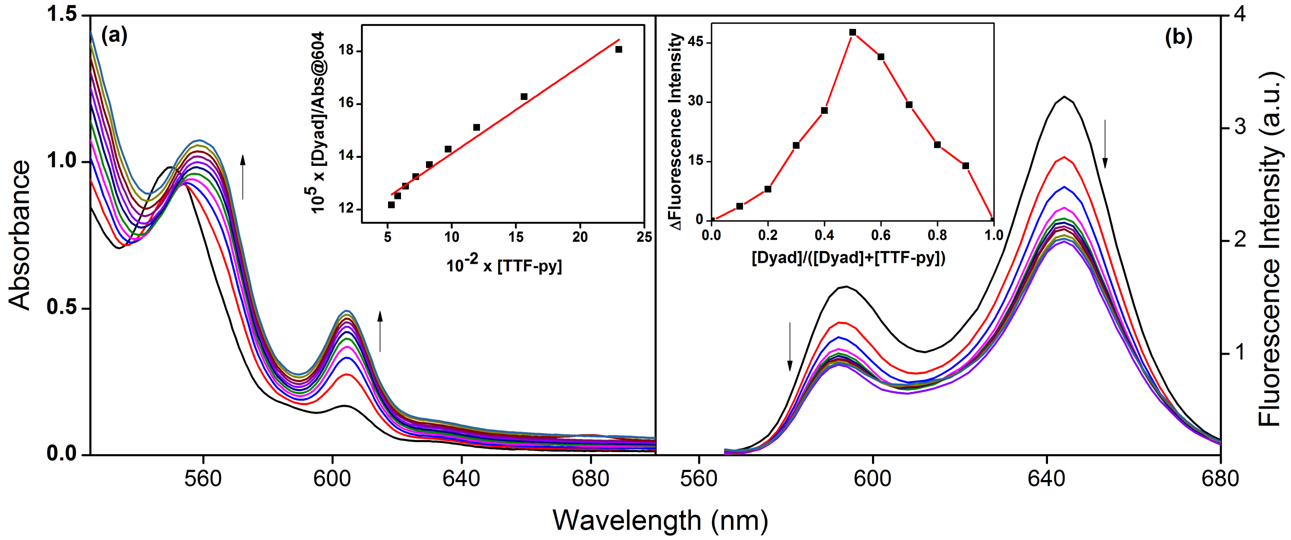

Fig. 4 Titrations of AlPor-Ph-AuPor$^+$ with TTF-py in dichloromethane. TTF-py was added up to 1.88 × 10^{-3} M in 20 µL (2.22 × 10^{-4} M) increments to 1 mL (6 × 10^{-5} M) solution of AlPor-Ph-AuPor$^+$. (a) Absorption titrations: Inset shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. (b) Fluorescence titrations: The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. The inset shows Job's plot where the total concentration of [AlPor-Ph-AuPor$^+$]+[TTF-py] was maintained constant at 4.2 × 10^{-5} M.

from the titrations of TTF-Ph-py *vs* AlPor-Ph-AuPor$^+$ (Fig. S10a) and found to be 3.5 × 10^3 M^{-1}. Titrations of TTF-py vs AlPor-Ph and TTF-Ph-py *vs* AlPor-Ph have been reported elsewhere.[50] Interesting trends were observed in *K* values. Titrations of TTF-py (or TTF-Ph-py) *vs* AlPor-Ph-AuPor$^+$ resulted in a higher degree of binding (≈3.3 × 10^3 M^{-1}) than that of TTF-py (or TTF-Ph-py) vs AlPor-Ph-H$_2$Por[52] (≈2.0 × 10^3 M^{-1}) and TTF-py (or TTF-Ph-py) vs AlPor-Ph[50] (≈1.0 × 10^3 M^{-1}). These results can be explained by the withdrawing nature of the axial subunit as it increases in order of Ph < H$_2$Por < AuPor$^+$. The Al center becomes a better Lewis acid and hence it binds strongly with Lewis base pyridine. Together with NMR and UV-visible absorption titrations, formation of the triads (TTF-py⟶AlPor-Ph-AuPor$^+$ and TTF-Ph-py⟶AlPor-Ph-AuPor$^+$) in dichloromethane solutions can be concluded.

4.4 Cyclic Voltammetry and Energetics

Cyclic voltammetry of newly investigated dyad and its reference compounds was measured in dichloromethane with 0.1 M TBAClO$_4$. Ferrocene was used as an internal standard. Representative voltammograms are shown in Fig. 5 and the data is summarized in Table 1. The redox processes of all the compounds are found to be one-electron reversible, based on the peak-to-peak separation values, and the cathodic-to-anodic peak current ratio. During the cathodic scan, dyad showed three reduction processes. Based on its monomers,

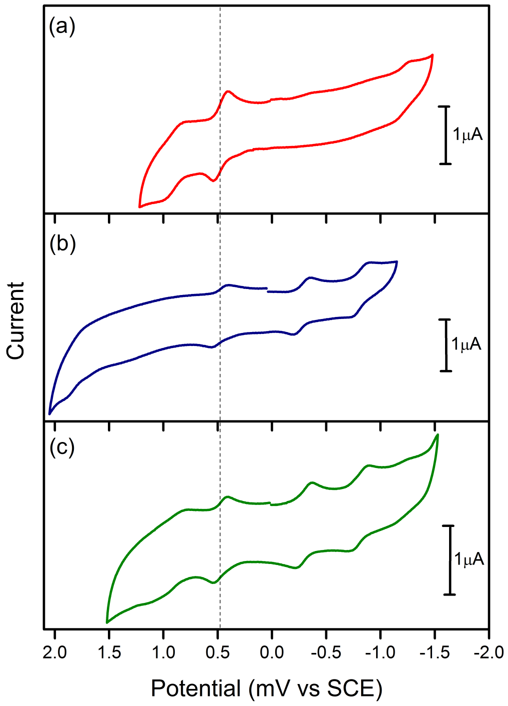

Fig. 5 Cyclic voltammograms of (a) AlPor-Ph, (b) AuPor$^+$-Ph and (c) AlPor-Ph-AuPor$^+$ with 0.1 M TBAClO$_4$ in dichloromethane. Data were measured with ferrocene as an internal standard. Note that the oxidation at 0.48 V in all voltammograms is due to the internal standard ferrocene. Scan rate 25 mV/sec.

the observed first two processes are assigned to the first and second reduction of axial AuPor$^+$ unit, whereas the third process is assigned to the first reduction of AlPor. While in anodic scan, dyad reveals two oxidation processes in our experimental conditions and are assigned to the AlPor. As anticipated, the dyad exhibited a combination of processes from its monomeric porphyrin units without any perturbation in their redox potentials. Thus, the observed cyclic voltammograms and redox data suggest that the porphyrin units of the dyad do not influence one another significantly. However, the redox potentials of AuPor$^+$-Ph shifted positively compared with its precursor pentafluorophenyl substituted free-base porphyrin (H_2Por-Ph).[52] This is due to the presence of positive charge (+3) on the Au centre, which make the porphyrin ring further electron deficient. Hence, AuPor$^+$ reduces at lower and oxidizes at higher potentials. The TTF derivatives (TTF-py and TTF-Ph-py) show two processes corresponding to the first and second oxidation of TTF moiety. These results have been published elsewhere.[50]

Fig. 6 shows the energy level diagram of the dyad and its corresponding supramolecular triads. The redox potentials are used in combination with optical data to estimate the energies of the radical ion pair states (E_{CS}) and free energy change for the charge separation (ΔG_{CS}) by using the Weller equation,[65, 66]

$$E_{CS} = e[E_{1/2}(D^{+\bullet}/D) - E_{1/2}(A/A^{-\bullet})] + G_S \qquad (1)$$

$$\Delta G_{CS} = E_{CS} - E_{0-0} \qquad (2)$$

where $E_{1/2}(D^{\bullet+}/D)$ is the first oxidation potential of the donor, $E_{1/2}(A/A^{\bullet-})$ is the first reduction potential of the acceptor and G_S is the ion-pair stabilization energy,

$$G_S = \frac{-e^2}{4\pi\varepsilon_0\varepsilon_S R_{D-A}} \qquad (3)$$

where $R_{D\text{-}A}$ is the centre-to-centre distance between the donor and acceptor,[67] ε_S is the dielectric constant of the solvent used for the optical and redox studies, in this case dichloromethane. The lowest excited singlet state energy ($E_{0\text{-}0}$) is estimated from the crossing point of absorption and fluorescence spectra and found to be 579 nm for AlPor.[52] Since AuPor was found to be non-fluorescent, the lower energy band maxima at 554 nm of absorption spectrum is taken as its lowest excited singlet state. The peak maxima of phosphorescence band at 769 and 752 nm for AlPor-Ph and AuPor$^+$-Ph, respectively (see Fig. 7) are used to estimate the lowest excited triplet states. The calculated free energy levels suggest that the lowest excited singlet state of AlPor (^{1}AlPor*) can be involved in electron transfer and hole transfer with AuPor$^+$ and TTF, respectively in the triad. However, the sequence of these processes depends on their rates. The calculated energy levels suggest that the triplet-triplet energy transfer from AuPor$^+$ to AlPor and triplet hole transfer from the excited triplet state [^{3}(AuPor$^+$)*] to AlPor are also energetically favourable. To verify these schemes, the steady-state fluorescence and the femtosecond transient absorption studies were performed.

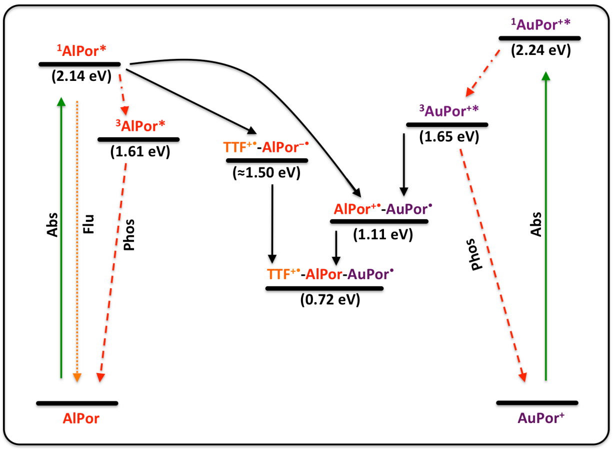

Fig. 6 Energy level diagram of the dyad and its corresponding supramolecular self-assembled triads in dichloromethane. Black solid lines represent electron transfer or hole transfer processes.

4.5. Fluorescence spectroscopy

Fig. 7 illustrates the fluorescence spectra of the dyad and its reference compounds in dichloromethane at room temperature and the data are summarized in Table 1. The AuPor$^+$ was found to be non-fluorescent at room temperature in our experimental conditions. This is due to the heavy atom effect induced by the Au(III) metal ion. As a result, the first excited singlet state of AuPor$^+$ [^{1}(AuPor$^+$)*] undergoes rapid intersystem crossing (ISC) to form the triplet state.[56] The dyad fluorescence was measured with excitation wavelength of 550 nm, where 80% of light is absorbed by AlPor. As shown in Fig. 7, the dyad revealed two fluorescence bands, which are similar to its reference molecule AlPor-Ph. However, their intensities are strongly (nearly 88%) quenched. Based on the energy level diagram (Fig. 6), where the ^{1}(AuPor$^+$)* is higher in energy than ^{1}AlPor*, and also due to a weak spectral overlap between AlPor emission and AuPor absorption (Fig. S11), the energy transfer from ^{1}AlPor* to AuPor$^+$ can be safely ruled-out. On the other hand, the electron transfer from ^{1}AlPor* to AuPor$^+$ is exergonic (ΔG_{CS}) by −1.03 eV. Therefore, the observed strong quenching is attributed to the electron transfer process. However, the heavy atom effect of Au metal cannot be neglected in the excited state properties.

Fig. 4b shows the fluorescence spectra of AlPor-Ph-AuPor$^+$ dyad with increasing amounts of pyridine-linked tetrathiafulvalene (TTF-py). The excitation wavelength was adjusted to the isosbestic point at 555 nm. In the absence of TTF-py, the dyad showed AlPor bands similar to its monomeric compound AlPor-Ph. However, their intensities were strongly quenched due to the electron transfer from ^{1}AlPor* to axial AuPor$^+$. Upon addition of TTF-py, the fluorescence bands of AlPor were further quenched. These notable spectral changes suggest the formation of TTF-py→AlPor-Ph-AuPor$^+$ triad in the solution. The complexation of AlPor-Ph-AuPor$^+$ with TTF-py in solution was determined by means of Job's plot based on the change in fluorescence intensity. Fig. 4b (inset) shows that a continuous variation plot of fluorescence intensity change vs

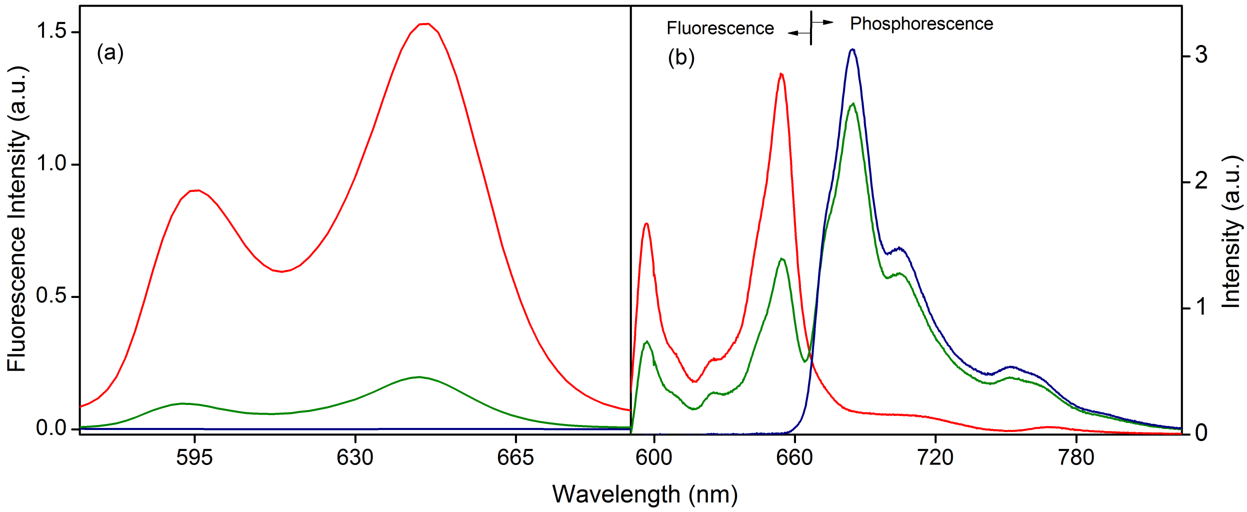

Fig. 7 Emission spectra of AlPor-Ph-AuPor$^+$ (green), AlPor-Ph (red) and AuPor$^+$-Ph (blue) in (a) dichloromethane at room temperature, excitation wavelength of 550 nm and (b) dichloromethane:ethanol (= 1:1) at 77 K, excitation wavelength of 520 nm.

[AlPor-Ph-AuPor$^+$]/([AlPor-Ph-AuPor$^+$]+[TTF-py]) in dichloromethane gave a maximal value of 0.5, indicating the formation of TTF-py→AlPor-Ph-AuPor$^+$ complex with a coordination ratio at 1:1. To explain the possible quenching mechanism, various control titrations, TTF *vs* AlPor-Ph-AuPor$^+$ (Fig. S12b) and pyridine *vs* AlPor-Ph-AuPor$^+$ (Fig. S13b), were carried out where no change in fluorescence intensity was observed. On the other hand, titrations of TTF-py (or TTF-Ph-py) *vs* AlPor-Ph revealed a strong quenching in fluorescence bands of AlPor due to the hole transfer from ^{1}AlPor* to TTF unit and these results are published elsewhere.[47, 50, 52] Thus, the most likely explanation for quenching in triad is an intramolecular photoinduced hole transfer from ^{1}AlPor* to TTF unit and this process was found to be exergonic (ΔG_{CS}) by −0.64 eV. Similar results were found from the titrations of TTF-Ph-py *vs* AlPor-Ph-AuPor$^+$ (i.e. formation of triad TTF-Ph-py→AlPor-Ph-AuPor$^+$, Fig. S10b). Due to an additional phenyl spacer between the TTF and py units, there is a decrease in the electronic coupling expected, which causes a slow down in hole transfer rate. Consistent with this expectation, the quenching is weaker. Therefore, the band shifts are more pronounced in the formation of triad TTF-Ph-py→AlPor-Ph-AuPor$^+$.

To investigate the possibility of hole transfer from ^{3}(AuPor$^+$)* to AlPor in the dyad, the steady-state fluorescence spectra were measured at low temperature. Fig. 7b shows the emission spectra of the dyad AlPor-Ph-AuPor$^+$ and its reference monomers AlPor-Ph and AuPor-Ph in dichloromethane:ethanol (1:1) at 77 K. Spectra were measured with excitation at 520 nm where 82% and 18% light is absorbed by AuPor$^+$ and AlPor, respectively. The AlPor-Ph showed fluorescence bands at 597 and 654 nm, as well as phosphorescence bands at 710 and 769 nm. In contrast, the AuPor$^+$-Ph displayed only phosphorescence bands at 685, 704 and 752 nm, which were overlapped with AlPor phosphorescence bands. As anticipated, the dyad showed combination of bands, which corresponds to the fluorescence and phosphorescence of AlPor and AuPor$^+$ entities. Furthermore, the fluorescence and phosphorescence bands are quenched by 51% and 14%, respectively. Based on the steady-state fluorescence studies at room temperature, it is reasonable to assign the quenching of AlPor fluorescence bands at 77K to the electron transfer from ^{1}AlPor* to AuPor$^+$. On the other hand, the singlet-singlet energy transfer from ^{3}(AuPor$^+$)* to AlPor and the hole transfer from ^{1}(AuPor$^+$)* to AlPor are not viable because gold(III) porphyrins are well known to have an extremely short-lived first excited singlet state.[57] In contrast, gold(III) porphyrins typically have a long-lived (usually 1-2 ns, see Ref. 52) excited triplet state. Therefore, in combination with suitable energy levels it is likely that the triplet-triplet energy transfer and triplet hole transfer from AuPor$^+$ to AlPor are possible in the investigated dyad at 77K. However, the results shown in Fig. 7b did not indicate any substantial evidence for these processes, i.e. the phosphorescence intensity of AuPor$^+$ was not varied significantly in presence of AlPor unit. Consequently, we can rule out the possibility of triplet-triplet energy transfer and triplet hole transfer from AuPor$^+$ to AlPor moiety.

4.6 Femtosecond laser flash photolysis

Femtosecond transient absorption studies were performed in *o*-DCB (instead of low boiling dichloromethane) to secure evidence of electron transfer and hole transfer processes in the dyad and triads. Samples were excited using 400 nm wavelength light where the absorbance ratio of AlPor and AuPor$^+$ is approximately 1:5. To help interpret the transient spectral data of charge separation products, spectroelectrochemical studies were performed on AuPor$^+$ in *o*-DCB, as shown in Fig. 8. The one-electron reduced product of AuPor$^+$ revealed peaks at 612, 645 (sh) and 790 nm. In addition, the Soret band of AuPor$^+$ located at 409 nm revealed a red-shift of 7 nm and appeared at 416 nm. These processes were found to be fully reversible. Spectroelectrochemical data of AlPor and TTF have been reported previously.[52]

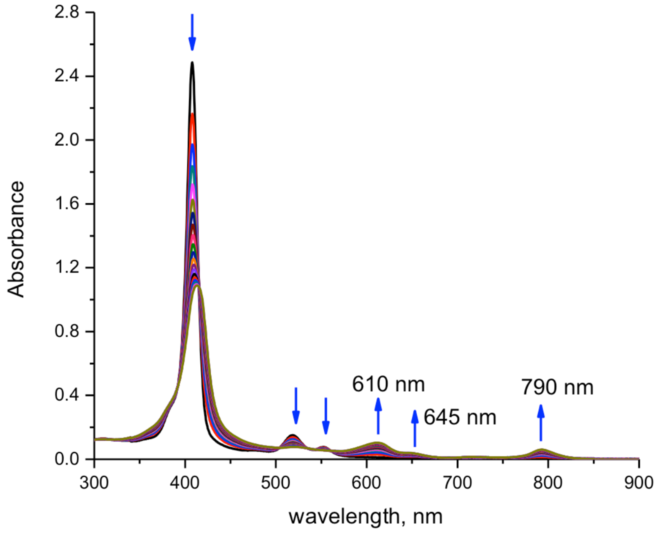

Fig. 8 Spectral changes observed during the first reduction of AuPor$^+$-Ph in *o*-DCB with 0.2 M TBAClO$_4$.

Fig. 9a shows the transient absorption spectrum of AuPor$^+$ at the indicated delay times. In agreement with literature results,[53] the instantly formed S$_1$ and S$_2$ states populated long-living triplet excited states via intersystem crossing process. Depleted bands at 520 and 552 nm corresponding to ground state bleaching of AuPor$^+$ and positive peaks at 585 and 628 nm were observed. Owing to very low fluorescence quantum efficiency, no strong peaks corresponding to stimulated emission of AuPor$^+$ was observed. As expected for the excited triplet state ^{3}(AuPor$^+$)*, the positive peaks decayed slowly as shown by the time profile of the 630 nm peak in the Fig. 9b. The decay rate constant was found to be 1.77 x 10^8 s^{-1} (time constant = 5649 ps) which could be considered as a lower limit since the decay process lasted beyond the monitoring time window of the instrument being 3 ns. The transient absorption spectrum of AlPor is shown Fig. S14, and it has been reported previously.[52]

Transient spectral features of AlPor-Ph-AuPor$^+$ dyad are shown in Fig. 10a where in addition to the singlet and triplet features of AlPor and AuPor$^+$, transient spectral features in the 612 nm range and at the 655 nm range (shoulder band to the main ^{3}(AuPor$^+$)* peak) corresponding to the formation of AuPor$^•$ and AlPor$^{+•}$, respectively, were clearly observed. That is, evidence for charge separation in the AlPor-Ph-AuPor$^+$ dyad resulting into the formation of AlPor$^{+•}$-Ph-AuPor$^•$ radical ion was established. This charge separation could originate from ^{1}AlPor* or ^{3}(AuPor$^+$)*, both having excited state energy sufficient to drive this process (Fig. 6). The earlier discussed phosphorescence studies revealed absence of significant quenching of ^{3}(AuPor$^+$)* in the dyad at 77 K (see Fig. 7b), however, at elevated temperature electron transfer could occur from this state as the transient peaks of ^{3}(AuPor$^+$)* decays faster in the dyad than in pristine AuPor$^+$. Additionally, no evidence for triplet-triplet energy transfer from ^{3}(AuPor$^+$)* to AlPor was observed indicating such a process is not competitive. By global fitting of the time profile of the 612 nm peak, time constants for charge separation and charge recombination were obtained. A rise time of 3.16 ps resulting

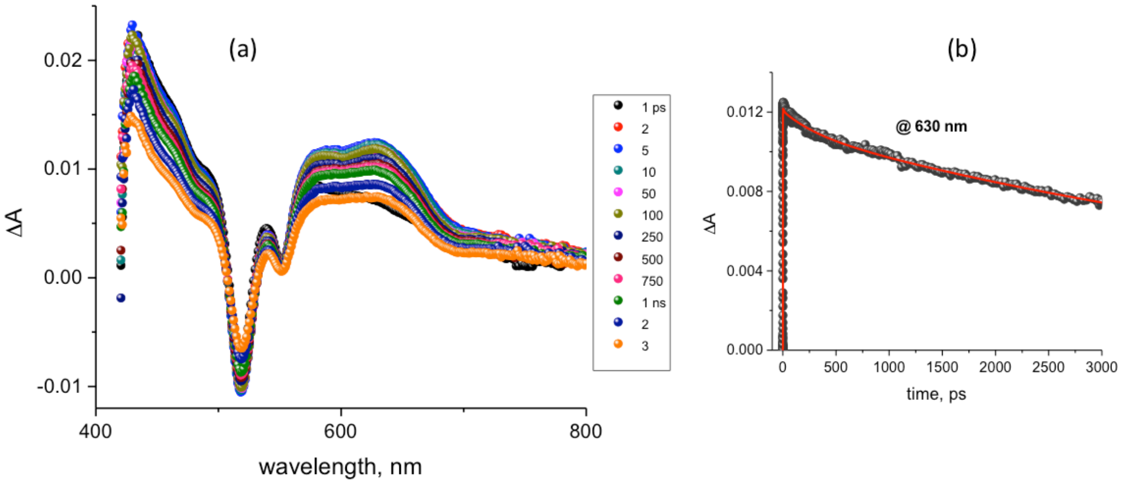

Fig. 9 Femtosecond transient absorption spectra of AuPor$^+$-Ph in *o*-DCB at the excitation wavelength of 400 nm.

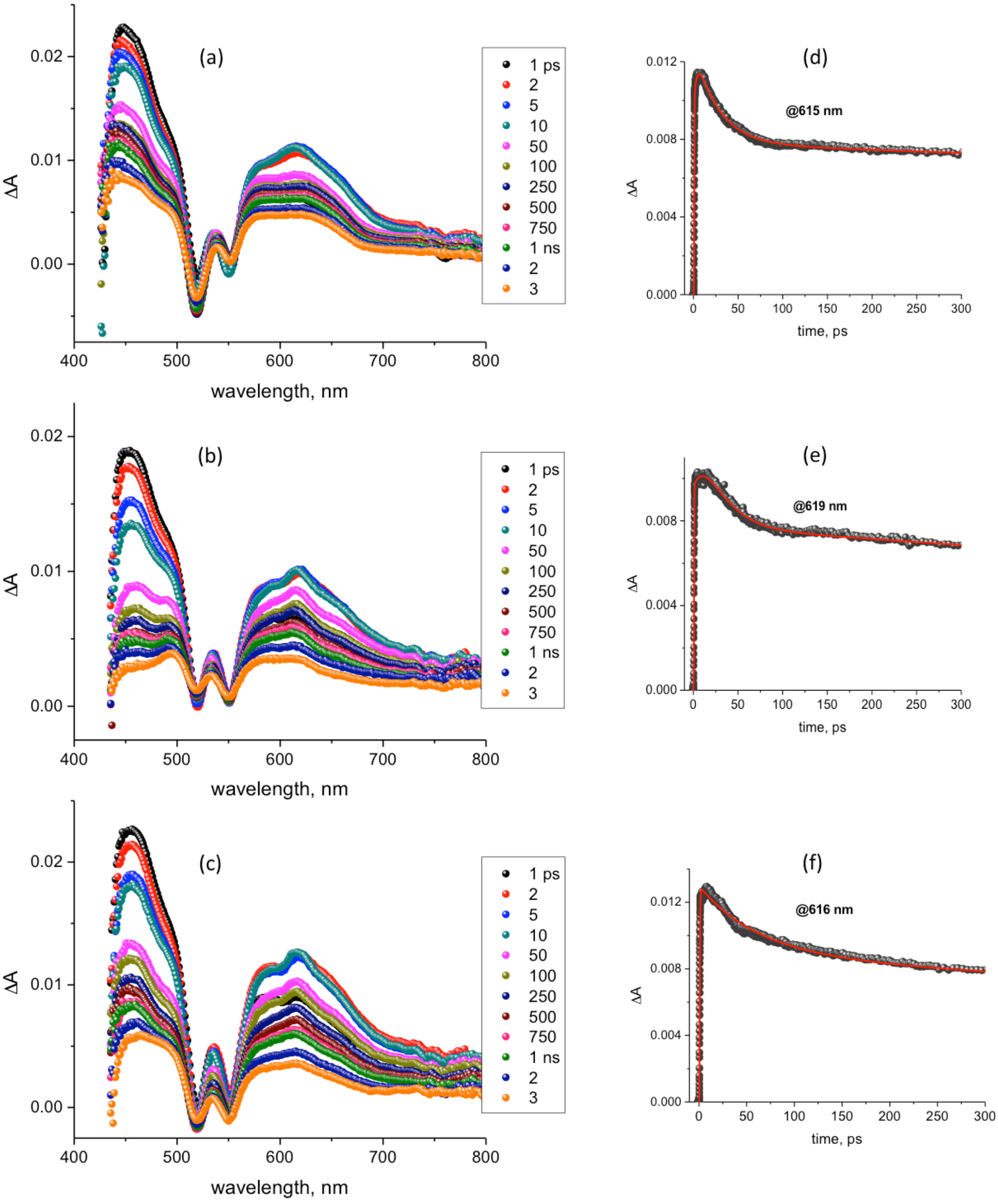

Fig. 10 Femtosecond transient absorption spectra of (a) AlPor-Ph-AuPor$^+$, (b) TTF-py →AlPor-Ph-AuPor$^+$ (3:1 ratio), and (c) TTF-Ph-py→AlPor-Ph-AuPor$^+$ (3:1 ratio) in *o*-DCB at the excitation wavelength of 400 nm. Figures d, e and f show the time profile of transient peaks of AlPor-Ph-AuPor$^+$, TTF-py →AlPor-Ph-AuPor$^+$ and TTF-Ph-py→AlPor-Ph-AuPor$^+$, respectively.

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into a rate of charge separation, k_{CS} = 3.17 x 10^{11} s^{-1}, suggesting occurrence of ultrafast charge separation in the dyad. However, the decay was found to be biexponential (Fig. 10d) with time constants of 27.26 and 2557 ps, resulting into rate of charge recombination, k_{CR} = 3.67 x 10^{10} s^{-1} and 3.91 x 10^{8} s^{-1}, respectively. The flexibility of the axially linked AlPor-Ph-AuPor^{+} dyad has been attributed as possible cause of the biexponential decay. It is important to mention here that due to the strong overlap of spectral features of AuPor$^{\bullet}$ and ^{3}(AuPor^{+})* in the 575-700 nm region, contributions of ^{3}(AuPor^{+})* in the long-living component cannot be ignored, although the time constant was lower than the time constant of pristine ^{3}(AuPor^{+})*.

Coordinating TTF-py or TTF-Ph-py to the Al centre of the dyad resulted in TTF-py→AlPor-Ph-AuPor^{+} and TTF-Ph-py→AlPor-Ph-AuPor^{+} triads. Fig. 10b and c show the femtosecond transient spectral data of these triads. In both spectra, peak at 612 nm corresponding to AuPor$^{\bullet}$ and at 650 nm corresponding to AlPor$^{+\bullet}$ and an additional peak in the 490 nm range corresponding to the formation of TTF$^{+\bullet}$ was observed. These observations are consistent with the formation of TTF$^{+\bullet}$-py→AlPor-Ph-AuPor$^{\bullet}$ and TTF$^{+\bullet}$-Ph-py→AlPor-Ph-AuPor$^{\bullet}$ distantly separated radical ion-pairs. By analysing the time profile of the 612 nm peak corresponding to AuPor$^{\bullet}$ by global fitting (Figs. 10e and f), time constants for charge separation and charge recombination were arrived. In the case of TTF-py→AlPor-Ph-AuPor^{+} triad, a rise time of 18.5 ps was obtained resulting into k_{CS} = 5.4 x 10^{10} s^{-1} while the biexponential decay with time constants of 1318 and 1468 ps resulted in k_{CR} values of 7.59 x 10^{8} s^{-1} and 6.81 x 10^{8} s^{-1}, respectively. For the TTF-Ph-py→AlPor-Ph-AuPor^{+} triad, the rise and decay time constants of the 612 nm peak were found to be 61.2 and 1484 ps resulting into k_{CS} of 1.64 x 10^{10} s^{-1} and k_{CR} of 6.74 x 10^{8} s^{-1}, respectively. For this triad, a monoexponential decay fit was satisfactory to evaluate k_{CR}.

The formation of the final charge separation product in the triads, TTF$^{+\bullet}$-py→AlPor-Ph-AuPor$^{\bullet}$ and TTF$^{+\bullet}$-Ph-py→AlPor-Ph-AuPor$^{\bullet}$ deserve special mention. There are at least two routes to form these species, viz.,

Route 1:
TTF-AlPor-AuPor^{+}⇒TTF-AlPor$^{+\bullet}$-AuPor$^{\bullet}$⇒TTF$^{+\bullet}$-AlPor-AuPor$^{\bullet}$
Route 2:
TTF-AlPor-AuPor^{+}⇒TTF$^{+\bullet}$-AlPor$^{-\bullet}$-AuPor^{+}⇒TTF$^{+\bullet}$-AlPor-AuPor$^{\bullet}$

In the first route, the initial photo process involves charge separation in AlPor-Ph-AuPor^{+} upon photoexcitation (originating either from ^{1}AlPor* or ^{3}(AuPor^{+})*) to yield AlPor$^{+\bullet}$-AuPor$^{\bullet}$ radical ion-pair. In the second step, AlPor$^{+\bullet}$ could undergo subsequent hole shift to TTF to yield the distinctly separated radical ion-pair, TTF$^{+\bullet}$-AlPor-AuPor$^{\bullet}$. In the second route, the initial step involves formation of TTF$^{+\bullet}$-AlPor$^{-\bullet}$ from ^{1}AlPor* state. In the subsequent step, electron migration from AlPor$^{-\bullet}$ to AuPor^{+} takes place to yield TTF$^{+\bullet}$-AlPor-AuPor$^{\bullet}$ radical ion-pair as the final product. The determined k_{CS} values by monitoring the time profile of AuPor$^{\bullet}$ for the triads are lower than that observed for the dyad but higher than the hole transfer rates from ^{1}AlPor* to TTF in the TTF-py→AlPor-Ph and TTF-Ph-py→AlPor-Ph control dyads (see Table 2).[52] These results suggest route 1 to be the main electron transfer mechanism. Importantly, k_{CR} values for the distinctly charge separated states of the triads were found to be about two orders of magnitude lower than that observed for the dyad in the absence of coordinated TTF. These results reveal successful charge stabilization in the self-assembled via axial position supramolecular triad.

4.7 Role of axial porphyrin (H_2Por vs AuPor^{+}) in dyads and triads

Noticeable differences were observed between the investigated compounds (AlPor-Ph-AuPor^{+} and TTF-Ph$_{n}$-py→AlPor-Ph-AuPor^{+}, n = 0, 1) in the present study and the compounds (AlPor-Ph-H_2Por and TTF-Ph$_{n}$-py→AlPor-Ph-H_2Por, n = 0, 1) that we recently studied.[48] The singlet-singlet energy transfer was found to be the main quenching mechanism in dyad AlPor-Ph-H_2Por where the axial porphyrin (H_2Por) acted as an energy acceptor. However, the role of H_2Por as an energy acceptor was modulated into an electron acceptor by introducing the electron rich TTF molecule to the dyad, that is

Table 2 Transient data of investigated compounds in *o*-DCB.

Sample	τ_{CS} (k_{CS})	τ_{CR} (k_{CR})
AlPor-Ph-AuPor^{+}	3.16 ps (3.12 × 10^{11} s^{-1})	27.26 ps (3.67 × 10^{10} s^{-1}), 2557 ps (3.91 × 10^{8} s^{-1})
TTF-py→AlPor-Ph-AuPor^{+}	18.5 ps (5.40 × 10^{10} s^{-1})	1318 ps (7.59 × 10^{8} s^{-1}), 1468 ps (6.81 × 10^{8} s^{-1})
TTF-Ph-py→AlPor-Ph-AuPor^{+}	61.2 ps (1.64 × 10^{10} s^{-1})	1484 ps (6.74 × 10^{8} s^{-1})
TTF-py→AlPor-Ph	80 ps (1.25 × 10^{10} s^{-1})	-
TTF-Ph-py→AlPor-Ph	120 ps (8.33 × 10^{9} s^{-1})	-

formation of triad TTF-Ph$_n$-py→AlPor-Ph-H$_2$Por.[52] In the presence of TTF, the ^{1}AlPor* state is rapidly quenched by the hole transfer to TTF unit before the transfer of excitation to H$_2$Por unit. The resulting primary radical pair TTF$^{+\bullet}$-Ph$_n$-py→AlPor$^{-\bullet}$-Ph-H$_2$Por ultimately undergoes a charge shift to H$_2$Por and generates a final radical pair TTF$^{+\bullet}$-Ph$_n$-py→AlPor-Ph-H$_2$Por$^{-\bullet}$. This way, the H$_2$Por entity in the triad was forced to participate as an electron acceptor rather than energy acceptor.

Interestingly, unlike the case of AlPor-Ph-H$_2$Por, photoexcitation of AlPor in the AlPor-Ph-AuPor$^+$ dyad resulted in electron transfer process from ^{1}AlPor* to the axial porphyrin (AuPor$^+$). The observed differences between the dyads (AlPor-Ph-H$_2$Por and AlPor-Ph-AuPor$^+$) can be explained by the changes that occur in optical and redox properties of the axial porphyrin (AuPor$^+$) due to gold(III) metalation. Upon gold(III) metalation, the spectral overlap between AlPor emission and AuPor$^+$ absorption decreases, which prevents the energy transfer process from ^{1}AlPor* to AuPor moiety. Moreover, facile reduction of AuPor$^+$ provides a large driving force for the electron transfer process from ^{1}AlPor* to AuPor$^+$ moiety. Together with these alterations, electron transfer becomes a favourable process between AlPor to AuPor$^+$ in newly synthesized AlPor-Ph-AuPor$^+$ dyad and its corresponding triads (TTF-py→AlPor-Ph-AuPor$^+$ and TTF-Ph-py→AlPor-Ph-AuPor$^+$). Therefore, upon excitation, the initial charge separation occurs predominantly between the AlPor and AuPor$^+$ units, which results in a primary radical pair (TTF-Ph$_n$-py→AlPor$^{+\bullet}$-Ph-AuPor$^\bullet$). In a consecutive step, the formed radical pair undergoes hole transfer to TTF unit to produce a spatially well-separated radical pair (TTF$^{+\bullet}$-Ph$_n$-py→AlPor-Ph-AuPor$^\bullet$, designated as route-1) with appreciable lifetimes.

5. Conclusions

The results presented above show the successful mimicking of vertical type photosynthetic reaction centre TTF-AlPor-AuPor$^+$ by exploiting the unique properties of AlPor, AuPor$^+$ and TTF entities. Ground state properties suggest that there are no intramolecular interactions between molecular components of the triads. However, due to a strong electron withdrawing nature of the axial AuPor$^+$, which induces Lewis acid-base interactions between the Al centre of AlPor and fluorine atom of counter ion PF$_6$, intermolecular interactions were found in the dyad. Optical studies revealed that the excitation of AlPor in the triad resulted in ultrafast charge separation predominantly from AlPor to AuPor$^+$ to generate the primary radical pair TTF-AlPor$^{+\bullet}$-AuPor$^\bullet$, which eventually undergoes hole transfer to yield the final radical pair TTF$^{+\bullet}$-AlPor-AuPor$^\bullet$. The resulting TTF$^{+\bullet}$-AlPor-AuPor$^\bullet$ radical pair in the triad has two orders of magnitude slower recombination than the recombination of its parent dyad, i.e. AlPor$^{+\bullet}$-AuPor$^\bullet$. Therefore, these results establish the successful charge stabilization in vertical type self-assembled 'D-AlPor-A' supramolecular triads.

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