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ARTICLE TYPE

Supramolecular Electron Donor-Acceptor Complexes Formed by Perylene Diimide Derivative and Conjugated Phenazines

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Novel electron acceptors are synthesized through methylation of dipyrido[3,2-a:2',3'-c]-7-aza-phenazine and dibenzo[a,c]-7-aza-phenazine. Absorption and fluorescence titration experimental results suggest that these phenazine derivatives may bind to aspartic acid modified perylene diimide (PASP) with moderate apparent association constant K_a (2.94×10^4 to 1.30×10^6 M^{-1}). Solvent polarity, electron accepting ability and the substituent of the phenazine derivatives all have important effect on the binding strength of PASP/phenazine complex. Photoinduced electron transfer from PASP to phenazine derivatives is confirmed by electrochemical, electron paramagnetic resonance (EPR) and time-resolved fluorescence experiments. The PASP/phenazine may form needle-like or rod-like nanostructures with lengths from 100 to 400 nm depending on their interaction model.

Introduction

Organization of molecules through non-covalent interaction is one of important ways to construct supramolecular assembly.[1] The electron-transfer complex with aromatic donor and acceptor units has received increasing attention.[2] However, the weak interaction between donor and acceptor molecules limits their potential applications in the creation of the organized structures with long-range order. Introduction of additional non-covalent interaction forces such as hydrogen bonding, electronstatic interaction, metal-ligand or anion coordination, and solvophobic forces has been used to enhance the stability of supramolecular donor-acceptor assembly.[3,4]

It has been reported that subtle variation of the structure of the building blocks may lead to significant changes in the molecular-level interaction and consequently the photophysical and electrochemical properties of the resulting assemblies.[5] A diverse range of electron-rich donors and electron-deficient acceptors with large π-surface have been applied in construction of donor-acceptor complexes. Perylene diimide derivatives (PDIs), with the advantage of chemical and photochemical stability and fluorescence quantum yield close to unity, have been used as prominent chromophore in organic solar cells,[6] dye lasers,[7] biological sensors and imaging[8], and field effect transistors.[9] PDIs have been extensively studied as electron-acceptor and have been used to construct charge transfer complexes.[10] Their rigid, large π-cores are particularly interesting for their ability to efficiently self-assemble into ordered nanostructures, including sphere-like, rod-like and vesicle-like structures.[11] However, the electron-donating properties of perylene dimimide derivatives have not been fully investigated.[12]

Pyridinium- and its analogues bipyridinium salts have been applied as electron acceptors in formation of interlocked compound,[13] bulk-level molecular electronic and nonlinear optical (NLO) materials.[14] The pyridinium derivatives with π-extended structure have shown rich redox behavior and unusual complexation mode,[15] which may provide opportunities for further design and construction of new supramolecular assemblies with specific structure and properties.[16] Recently, some quaternarized dipyrido [3,2-a:2',3'-c]-phenazine derivatives with pyridinium groups have been synthesized,[17] and the cationic phenazine shows rather high reduction potential (E_{red} = -0.16 V vs NHE), suggesting that these cationic phenazine derivatives may act as electron acceptor.[18] Dipyrido[3,2-a:2',3'-c]-7-aza-phenazine (**2a**, Scheme 1) possesses similar reduction potential (-0.142 V vs SCE) to that of cationic phenazine, and photoinduced electron transfer reaction between **2a** and DNA can occur.[19] In this study, two cationic phenazine derivatives are synthesized through methylation of **2a** and dibenzo[3,2-a:2',3'-c]-7-aza-phenazine (**2b**), respectively, which exhibit higher reduction potential than **2a**. These phenazine derivatives can serve as electron acceptor, and form stable charge-transfer complex with PASP through multiple interactions. The photophysical properties and nanostructure of PASP/phenazine complexes are investigated in detail.

Experimental Methods

Chemicals and instruments.

1,10-Phenanthroline, phenanthrenequinone, 3,4,9,10-perylenetetracarboxylic dianhydride, 3,4-pyridinediamine, aspartic acid, iodomethane, methyl viologen and tris(hydroxymethyl)aminomethane (Tris) were purchased from TCI company (Tokyo, Japan). Water was freshly distilled twice

before use. All experiments involving buffer solution were performed in 10 mM Tris–HCl (pH 7.4), unless otherwise noted.

Compound **1a** (1,10-phenanthroline-5,6-dione),[20] **2a** (dipyrido[3,2-a:2',3'-c]-7-aza-phenazine, dpapz),[21] N,N'-Di(2-succinic acid)-perylene-3,4,9,10-tetracarboxylic bisimide (PASP) [22] were prepared according to literature procedures.

NMR spectra were recorded with a 500 MHz spectrometer for ^{1}H NMR, 125 MHz for ^{13}C NMR. Chemical shifts δ are given in parts per million (TMS as internal standard). Steady state absorption and fluorescence spectra were recorded with a Hitachi UV-3010 UV−Vis spectrophotometer and Hitachi F-4600 spectrofluorimeter, respectively. The nanostructurs were imaged using TEM (JEOL, Ltd., Japan; JEOL-2010) at an acceleration voltage of 120 KV.

Cyclic voltammetry (CV) experiments were performed on a CHI660D electrochemical workstation, using two platinum wires as the working and counter electrodes, respectively, and a saturated calomel electrode (SCE) as the reference electrode in the presence of 1 mM n-tetrabutylammonium perchlorate as supporting electrolyte.

EPR spectra were obtained using a Bruker ESP-300E spectrometer operating at room temperature, and the operating conditions were the following: microwave bridge, X-band with 100 Hz field modulation; sweep width, 200 G; receiver gain, 1×10^5; microwave power, 5 mW. Samples were injected into the specially made quartz capillaries for EPR analyses, purged with argon or air for 30 min in the dark, respectively, according to the experimental requirements, and illuminated directly in the cavity of the EPR spectrometer with a Nd:YAG laser (355 nm) except as noted elsewhere.

Synthesis of dibenzo[a,c]-7-aza-phenazine (2b)[23]

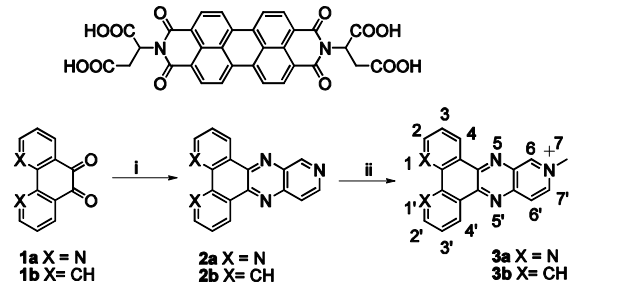
0.5 g phenanthraquinone (**1b**) (2.4 mmol) and 0.5 g 3,4-diaminopyridine (4.5 mmol) were dissolved in 50 mL of dried ethanol and refluxed under N_2 atmosphere for 6 h. After cooling to room temperature, yellow solid was obtained. The crude product was collected by filtration and washed with ethanol several times, to yield **2b** as pale yellow solid (0.64 g, 95%). ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 9.74 (s, 1H); 9.32 (d, J = 7.8 Hz, 2H); 8.86 (d, J = 5.4 Hz, 1H); 8.51 (m, 2H); 8.10 (d, J = 5.4 Hz, 1H); 7.83 (m, 2H); 7.73 (m, 2H).

General procedure for the preparation of 3a and 3b

A solution of CH_3I (1.53 g, 10.9 mmol) in 5 mL of chloroform was added dropwise to a solution of **2a** or **2b** (1.6 mmol) in 10 mL of dry chloroform. The mixture was refluxed under N_2 atmosphere for 24 h. The precipitate was separated and washed with chloroform to yield a wine-red solid.

Synthesis of N-methyl dipyrido[a,c]-7-aza-phenazine (3a) (0.625 g, yield 90%): ^{1}H NMR (DMSO-d_6, 500 MHz) *δ*: 10.61 (s, 1H); 9.61 (d, J = 7.5 Hz, 1H); 9.53 (d, J = 7.5 Hz, 1H); 9.37 (m, 2H); 9.184 (d, J = 7.0 Hz, 1H); 8.99 (d, J = 6.5Hz, 1H,); 8.08 (m, 2H) ; 4.71 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) *δ*: 155.26, 154.52, 153.55, 150.21, 149.48, 149.32, 146.48, 145.79, 141.33,136.60, 135.26, 134.22, 126.76, 126.73, 126.69, 125.81, 125.69, 49.02. HRMS (ESI) (m/z): $[M-I^-]^+$ calcd for $C_{18}H_{12}N_5$, 299.1126; found, m/z 299.1168.

Synthesis of N-methyl dibenzo[a,c]-7-aza-phenazine (3b) (0.620 g, yield 89%)^{1}H NMR (DMSO-d_6, 500 MHz) *δ*: 10.45 (s, 1H); 9.21 (m, 1H); 9.08 (m, 2H); 8.79 (m, 2H); 8.61 (s, 1H); 7.99 (m, 2H); 7.76 (m, 2H); 4.68 (s, 3H). ESI-MS (m/z): $[M-I^-]^+$ 296.1, calcd for $C_{20}H_{14}N_3$, 296.1



Scheme 1 Molecular structure of PASP and synthetic route of **3a-b**. Reagents and conditions: (i) 3,4-pyridinediamine, ethanol, reflux for 6 h; (ii) iodomethane, chloroform, reflux for 24 h

Fluorescence Titration

The titrations were performed by adding the required volumes of a solution of phenazine derivative (1 mM) into the solution of PASP (4 μM). Under experimental conditions, the fluorescence of PASP decreased with increasing phenazine derivative concentration. According to eqn (1),

PASP + phenazine →PASP/phenazine (1)

The apparent association constant (K_a) of the formed PASP/phenazine complex could be determined using the nonlinear least squares method according to the curve fitting in eqn(2). [24]

$$F_0 - F = \{\alpha([PASP]+[phenazine]+1/Ka) - \sqrt{\alpha^2([PASP]+[phenazine]+1/Ka)^2 - 4\alpha^2[PASP][phenazine]}\}/2 \quad (2)$$

Where F_0 and F were the fluorescence of PASP at given wavelength in the absence and presence of phenazine derivative and α was the proportionality coefficiencent, which may be taken as a sensitivity factor for the fluorescence change induced by the addition of one molar electron acceptor.

Results and discussion

Synthesis and characterization

Both pyridinium and phenazine derivatives can act as electron acceptors to construct donor-acceptor assemblies. It can be anticipated that the electrophilicity can be enhanced by conjugation of pyridinum and phenazine moeities.[17,18] Scheme 1 shows the chemical structures and synthetic routes for quaternarized phenazine derivatives **3a** and **3b**. The positive ESI-HRMS mass spectrum of **3a** reveals a molecular ion peak at m/z 299.1168 $[M-I^-]^+$ (Fig. S1a), in consistence with the molecular formula $C_{18}H_{12}N_5$ (required 299.1126 for $C_{18}H_{12}N_5$), suggesting that N-methylated pyridinium is formed. Due to the existence of multiple nitrogen atoms in **3a**, ^{1}H and ^{13}C NMR experiments are carried out to verify the chemical structure of **3a**. All the aromatic proton signals of **3a** undergo significant downfield shift compared with that of **2a** (Fig. 1). The alkylation of nitrogen atom in position N-7 of **2a** is designated according to the analysis of 1D and 2D NMR spectra of **3a**, including HSQC (Fig. 2), ^{1}H-^{1}H COSY (Fig. S1b) and HMBC (Fig. S1c). It has been reported that the

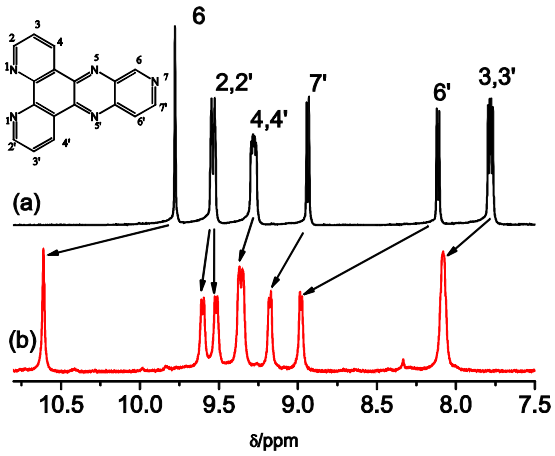


Fig. 1 ^{1}HNMR spectra of (a) **2a** and (b) **3a**. Inset: the chemical structure of **2a**.

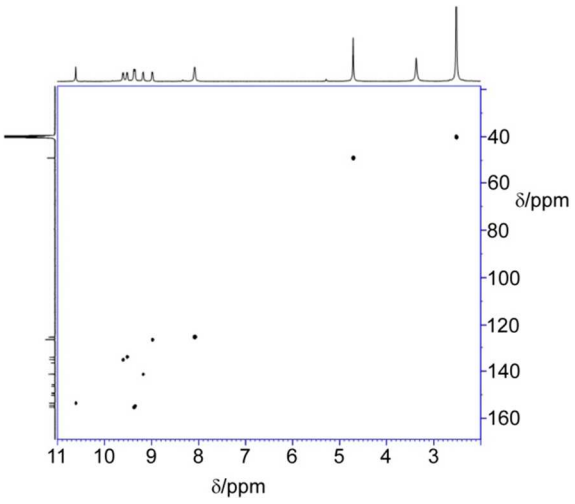


Fig. 2 HSQC NMR spectra of **3a**.

heterocyclic diquaternary salt of dppz can be formed by alkylation with ethylene dibromide under reflux condition.[25] Maybe due to relatively low reaction temperature (50 °C) employed in our experiment, the nitrogen atoms in position N-1 and N-1' of **2a** remain unchanged. Another quaternary pyridinium **3b** is characterized with ^{1}H NMR and ESI-MS.

UV-Vis and fluorescence titration

Phenazine derivatives can be used as electron-withdrawing moieties to construct electron acceptor-donor system.[26] The compounds **2a-b** and **3a-b** exhibit moderate absorbance and emission in UV-Vis region (Fig. S2 and Table S1). Assembly formation between PASP and phenazine derivatives has been examined by steady-state absorption and emission spectroscopy. In buffer solution, PASP exhibits two absorption peaks at 496 and 532 nm (Fig. 3a). Addition of **2a** to the solution of PASP leads to hypochromic changes with the value of 23.5% and a red shift of the absorption maximum from 532 to 538 nm. In addition, the absorption of PASP in the presence of **2a** shows one isosbestic point at 439 nm. These results indicate that **2a** can

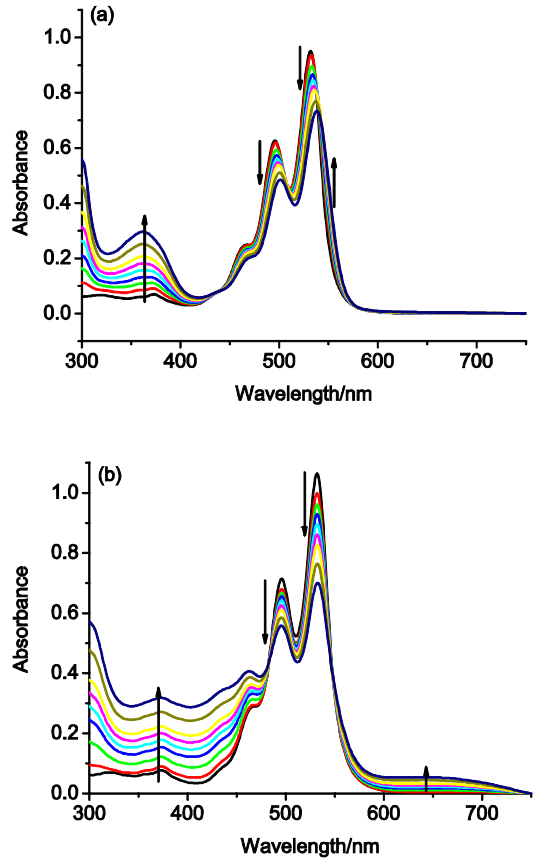


Fig. 3 UV-Vis spectral changes of PASP (16 μM) in the presence of (a) **2a** and (b) **3a** in Tris-HCl buffer solution (10 mM, pH 7.4). [**3a**] = [**2a**] = 0, 4, 8, 12, 16, 20, 24, 32, 40 μM.

associate with PASP through π-π stacking interaction.[27] Addition of **3a** to the solution of PASP brings about a considerable hypochromicity in the absorption spectra of PASP, with isosbestic points at 483 and 548 nm, suggesting that **3a** and PASP can form stable complex (Fig. 3b). The broad absorption bands at 370 and 650 nm originate from the addition of **3a**. However, no red-shift in the absorption spectra of PASP can be observed upon addition of **3a**, indicating that **3a** may associate with PASP mainly through electrostatic interaction.[28] The steric hindrance effect of the methyl group in **3a** may destabilize the stacking between **3a** and PASP by reducing the stacking surface.[29]

Along with the UV−Vis spectral changes, a decrease in the fluorescence intensity of PASP is observed upon addition of **2a** and **3a-b**. The emission spectrum of PASP shows a band with a maximum at 549 nm in DMSO-buffer solution (Fig. 4a) and 551 nm in buffer solution (Fig. 4b). Titration of PASP with **3a** leads to fluorescence quenching (Fig. 4a and b). The apparent binding constant (K_a) between PASP and phenazine derivatives can be calculated by analyzing the sequential changes in fluorescence intensity of PASP at varying concentrations of phenazine (eqn(2)) (Fig. 4c and d). For each phenazine derivative (**2a** and **3a-b**) examined, the plot of F_0-F as a function of phenazine concentration gives an excellent fit ($R^2 > 0.994$), verifying the

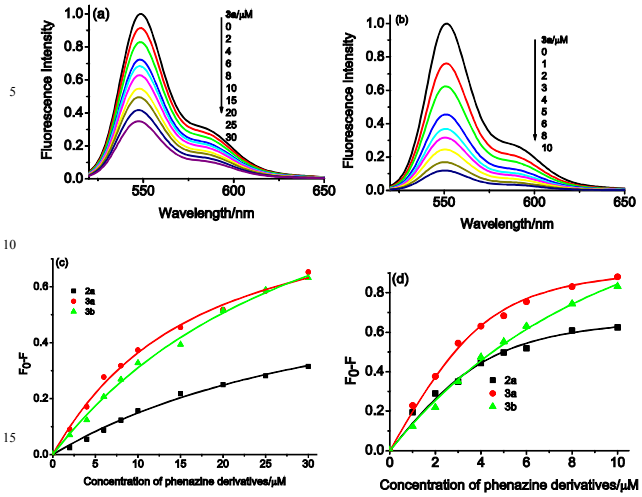


Fig. 4 Fluorescence emission spectra of PASP (4 μM) in (a) DMSO-buffer solution (1/1, v/v, pH 7.4) and (b) buffer solution (pH 7.4) containing different concentration of **3a**. Differential fluorescence intensity of PASP used to calculated K_a in (c) DMSO-buffer solution (1/1, v/v, pH 7.4) and (d) buffer solution (pH 7.4) by nonlinear least-squares curve-fitting analysis.

Table **1** Association Constants (K_a, M^{-1}), redox potentials of compounds and the calculated results of the free energy changes (ΔG) of photoinduced electron transfer reactions involving PASP and electron acceptors

Compound	association constant		E_{red} (V vs SCE) [a]	ΔG(ev)
	DMSO-buffer	buffer		
3a	7.46×10^4	1.30×10^6	-0.177	-0.413
3b	3.49×10^4	1.32×10^5	-0.296	-0.294
2a	2.94×10^4	1.05×10^6	-0.552	-0.038
2b	N.D[b]	N.D	-0.674	0.084
MV	N.D	N.D	-0.68[c]	0.090

[a]Cyclic voltammograms were measured in DMSO-buffer solution (1/1, v/v) with 0.1 M n-terabutoxyammonium percholate as the supporting electrolyte. [b]N.D means not detectable. [c]Data reported in literature.[34]

validity of the 1:1 complex stoichiometry. The association constants K_a between PASP and phenazine derivatives are summarized in Table 1. The association constants K_a are in the range of 2.94×10^4 to 1.30×10^6 M^{-1}, similar to the values obtained for the complexation of perylene diimide with porphyrin.[30] The association constant of PASP/phenazine complex in buffer solution is much larger than that in relatively low-polar DMSO-buffer solution. Considering the fact that water can bind the polar and charged moiety of **3a** and **3b** and weaken the electrostatic forces in PASP/**3a** and PASP/**3b**, the enhanced association of PASP/phenazine in buffer solution may mainly arise from hydrophobic interaction in PASP/phenazine complex.[31] The supramolecular assembly, which is driven by multiple interactions including hydrophobic interaction and electrostatic interactions, possesses high stability even in aqueous solution.[32] Both in DMSO-buffer solution and buffer solution, **3a** shows relatively higher affinity to PASP than **3b,** suggesting elegant structural design is important for supramolecular assembly. While changing the solvent from DMSO-buffer to pure buffer, the association constant between **2a** and PASP increases from

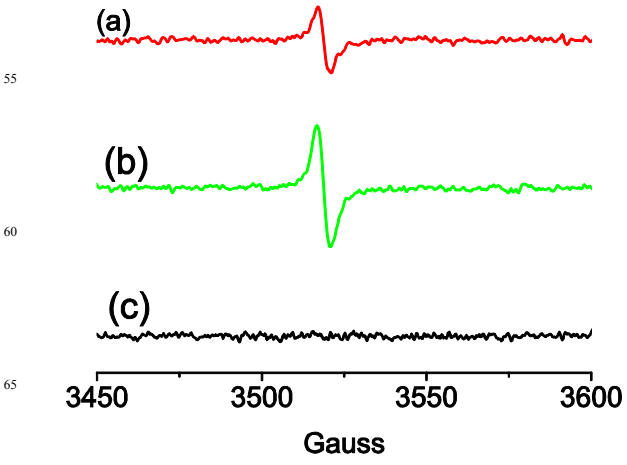


Fig. 5 Photoinduced EPR spectra of deoxygenated solution of **3a** (0.5 mM) in the presence of (a) PASP (0.5 mM) and (b) triethylamine (0.5 mM) in DMSO-buffer solution (v/v, 1/1, pH 7.4) upon irradiation at 355 nm for 30 s. (c) Photoinduced EPR spectrum in the absence of **3a**, PASP or light.

2.94×10^4 M^{-1} to 1.30×10^6 M^{-1}, which can be attributed to the strong hydrophobic interaction and solvophobic forces in alternate D-A π-stacking complex in buffer solution.[33]

In principle, both energy transfer and electron transfer processes could be considered to be responsible for the fluorescence quenching of PASP. However, the maximum fluorescence peaks of phenazine derivatives appear at shorter wavelength than that of PASP (Fig. S2), indicating that the energies of the singlet states of phenazine derivatives are higher than that of PASP, thus ruling out the possibility of energy transfer.

Cyclic voltammetric studies are performed to visualize the redox property and the free energy (ΔG) of intermolecular electron transfer from excited state PASP to phenazine derivatives is estimated by Rehm-Weller equation (eqn(3)).

$$\Delta G = E_{ox}(\text{donor}) - E_{red}(\text{acceptor}) - E_{0\text{-}0}(\text{Excited state energy}) \quad (3)$$

where E_{ox}(donor) is the oxidation potential of the donor PASP (1.66 V Vs SCE),[35] E_{red}(acceptor) is the reduction potential of the acceptor phenazine derivative (Table 2). $E_{0\text{-}0}$ is the singlet excited energy of PAPS (2.25 ev), calculated from the formula $E_{0\text{-}0} = 1240/\lambda_{em}$ (λ_{em} = 549 nm) (Fig. 4a).[36]

The calculated free-energy ΔG for electron transfer from the excited PASP to **2a** or **3a-b** is found to be exergonic (ΔG < 0) (Table 1). These results suggest that electron transfer from excited-state of PASP to **2a** or **3a-b** may occur. On the other hand, the intermolecular electron transfer from singlet excited state PASP to compound **2b** or traditional electron acceptor methyl viologen (MV) is thermodynamically unfavorable process (ΔG > 0), maybe due to more negative reduction potential of **2b** and MV. The UV-Vis and fluorescence emission spectra of PASP are not affected by the addition of **2a** or MV (data not shown). The above results demonstrate that the electrochemical properties of electron acceptor are important for constructing electron donor-acceptor assembly with PASP.

EPR and fluorescence lifetime quenching studies

To obtain further insight into the mechanism of photoinduced

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Table 2 Fluorescence life time (τ_f), electron transfer rate constants k_{ET} ($\times 10^8$ s^{-1}), and electron transfer quantum yields Φ_{ET} (s^{-1}) for PASP in the absence and presence of electron acceptors

compound	DMSO-buffer			buffer		
	τ_f/ns(fra %)	k_{ET}	Φ_{ET}	τ_f/ns(fra %)	k_{ET}	Φ_{ET}
PASP	3.71			4.40		
PASP/**2a**	3.71 (71.7%)	0.16	0.06	4.40 (68.9%)	0.58	0.20
	2.97 (28.2%)			1.50 (31.1%)		
PASP/**3a**	3.71 (24.1%)	1.72	0.38	4.40 (21.8%)	4.71	0.67
	1.80 (75.9%)			0.60 (78.2%)		
PASP/**3b**	3.71 (55.7%)	0.48	0.15	4.40 (23.9%)	2.36	0.51
	2.44 (44.3%)			1.45 (76.1%)		

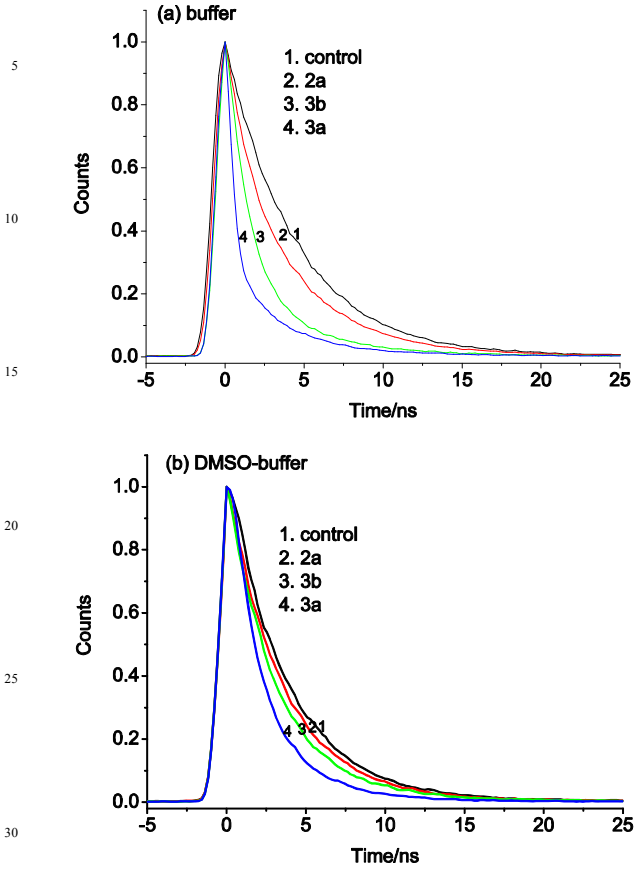

Fig. 6 Fluorescence decay profiles of PASP (4 μM) in (a) Tris-HCl buffer solution (10 mM, pH 7.4) and (b) DMSO-buffer solution (10 mM, pH 7.4, 1/1, v/v) in the presence of **2a**, **3a** or **3b**. (λ_{ex} = 496 nm)

electron transfer in PASP/phenazine complex, EPR technique is employed. Upon irradiation of the mixture of **3a** and PASP in argon-saturated DMSO-buffer solution, an EPR signal could be observed (Fig. 5a). The g factor is 2.003, which is close to the value of 10-methylacridine radical ($AcrH^{\cdot}$),[37] indicating that this signal arise from the reduction of **3a**. When **3a** was irradiated in the presence of triethylamine, a strong electron donor, a remarkable increase in the intensity of EPR signal is observed (Fig. 5b). This observation further supports the assignment of this EPR signal to the radical of **3a**. Control experiments confirm that **3a**, PASP and light are all necessary to produce the reduction radical of **3a** (Fig. 5 c). The above results prove the possibility of photoinduced electron transfer from PASP to **3a**. Due to the strong oxidation ability of PASP, it is difficult to detect the radical cation of PASP in aqueous solution.[38]

Fig. 6 shows the fluorescence decay time profiles of PASP and its complexes with **2a** and **3a-b**. The decay curve for PASP can be fitted monoexpoentially with lifetime of 4.40 ns in buffer solution and 3.71 ns in DMSO-buffer solution. The fluorescence time profiles of PASP in the presence of **2a** or **3a-b**, could be fitted satisfactorily to biexponential decay. The longer lifetime component can be assigned to the singlet state of pristine PASP and the shorter time component maybe due to photoinduced electron transfer from the singlet excites PASP to **2a** or **3a-b**. The rate constant (k_{ET}) and the efficiency (Φ_{ET}) for the electron transfer can be calculated from the lifetimes of PASP $(\tau_f)_{PASP}$ and the average lifetime of its complexes $(\tau_f)_{complex}$ according to Eqn.(4) and (5), respectively, which are all summarized in Table 2.

$$K_{ET}^{singlet} = 1/(\tau_f)_{complex} - 1/(\tau_f)_{PASP} \quad (4)$$

$$^{b}\Phi_{cs} = [(\tau_f)_{PASP} - (\tau_f)_{complex}]/(\tau_f)_{PASP} \quad (5)$$

The data in Table 2 show that both the trends of the k_{ET} and Φ_{ET} are **3a** > **3b** > **2a**, in agreement with the trend of reduction potential of **3a**, **3b** and **2a** (Table 1). PASP/**2a** and PASP/**3a** have similar binding constants in buffer solution (Table 1), while the Φ_{ET} value decreases from 0.51 for PASP/**3a** to 0.20 for PASP/**2a**. For the same phenazine derivative, the Φ_{ET} value in DMSO-buffer is much lower than that in buffer solution, which indicates that solvent may influence the efficiency of electron transfer.[39]

Transmission Electron Microscopy (TEM)

Perelene diimide derivatives are selected as important building blocks for self-assembly on the basis of geometry (strong π-π interaction) and function (optoelectronic properties).[40] The interaction behavior of PASP with phenazine derivatives has been studied by transmission electron microscopy (TEM). As shown in Fig. 7a and b, PASP shows irregular nanostructure, probably due to electrostatic repulsion of negatively charged PASP heads.[41]

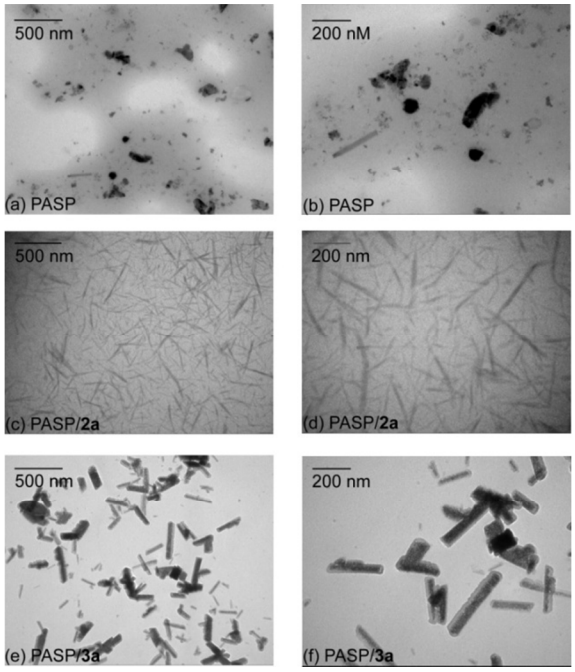

Fig. 7 TEM image of PASP (a, b), PASP/**2a** (c, d) and PASP/**3a** complex (e, f) prepared in buffer solution (pH 7.4). [PASP] = [**2a**] = [**3a**] = 50 μM.

TEM of PASP/**2a** complex shows the formation of 1-D needle-like nanostructures with the length of 100-400 nm (Fig. 7c and d). It has been reported that the donor-acceptor complex of PDI can form needle-like nanostructure through attractive intermolecular hydrophobic interactions and the stacking of the aromatic core.[42] As for PASP/**3a**, rod-like nanostructure can be observed with an average diameter of about 40-75 nm, and the average length of about 170-400 nm (Fig. 7e and f). Based on the electrostatic interactions between the positive charged head groups of **3a** and negative charged head group of PASP, PASP/**3a** can aggregate in rod-like nanostructure through layer-by-layer growth manner.[43]

Conclusions

In conclusion, we have synthesized two novel electron acceptors with phenazine moiety, which can form electron donor-acceptor complexes with aspartic acid modified perylene diimide. The solvent polarity has remarkable effect on the binding model and association constant of perylene diimide/phenazine complex. Moderate electron transfer quantum yields (Φ_{ET}) from singlet excited aspartic acid modified perylene diimide to phenazine derivatives can be observed and the photoinduced electron transfer in perylene diimide/phenzaine complex is further confirmed with EPR experiments. Needle-like and rod-like nanostructures of perylene diimide/phenzaine complex are formed by coassembly of donor and acceptor molecules through multiple interactions.

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