Two-path photo-induced electron transfer in naphthalimide-based model compound

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A photo-induced electron transfer (PET) model compound in the form acceptor–fluorophore–donor and its reference compounds were synthesized. Because the fluorescence of the fluorophore 4-amino-1,8-naphthalimide (ANI) was quenched by any PET process from donor to fluorophore (PET input path) or from fluorophore to acceptor (PET output path), therefore, if one of the above two paths was switched off, the occurrence of the PET process *via* the other PET path could be investigated by the fluorescence behavior of 4-amino-1,8-naphthalimide. Thus, the two-path PET in the model compound could be probed individually through the fluorescence signal of 4-amino-1,8-naphthalimide. Switching off the PET input path could be achieved by protonation (or quaternization) of the tertiary amine donor. The intramolecular electric field, which forced the electron transfer to proceed *via* the output path, could be destroyed through symmetrization of the model compound by the introduction of an identical amine substituent on the non-substituted 1,8-naphthalimide acceptor. It is worth noting that once either of the paths was of the status of "on", PET occurred and the fluorescence signal of 4-amino-1,8-naphthalimide was quenched.

Introduction

In recent years, photo-induced electron transfer (PET), as one of the most intriguing processes occurring in the photosynthesis reaction center (PRC), has attracted much attention from chemists for establishing synthetic models for pursuing deep comprehension of this phenomenon. Many supramolecular compounds have been developed as PET models to mimic and probe the PET process in PRC.[1–4] Furthermore, it is of importance to carry out the study of PET because it provides a basis for the design of molecular electronic devices.[5] Generally, PET model compounds are constructed in the form receptor–spacer–chromophore, in which the receptor is a reactive group *e.g.*, tertiary amine, crown ether, or boronic acid, *etc.*[6–10] The chromophores used in such models may be either the ones that are found in natural systems, *e.g.*, chlorophyll, pheophytins and quinones,[1–4,11,12] or specific artificial molecules, which are known to be efficient electron donors and acceptors, *e.g.* naphthalimide derivatives.[5,13–16]

However, the PET in bacterial PRC is a much more complex system after all. In fact, within the reaction center, it involves not only electron input from the antenna system to chlorophyll but also electron output from chlorophyll to primitive acceptor. Therefore, to mimic and probe the essential features of the PET process in the reaction center, it is necessary for the designed PET models to be constructed in an integrated format, which involves not only electron input from donor to chromophore but electron output from chromophore to acceptor.[17] Moreover, it is more important to make each PET step in the designed model compounds detectable. In other words, the "on" and "off" status of the electron transfer pathway should be exhibited through an obvious signal. Thus, the factors which orient and force the electron transfer and the relations between each component, could be exploited unambiguously.

Molecular switching by an external stimulus is one of the fundamental methods used to control and analyze the various parameters which govern PET model compounds. Protonation can act as an external trigger in the PET models containing basic groups. In the patterns based on 1,8-naphthalimide derivatives, protonation has been shown to switch the paths of PET, and the orientation of electron transfer is determined by the photogenerated intramolecular electric field resulting from the dipole moment in the excited state.[8,10,18,19]

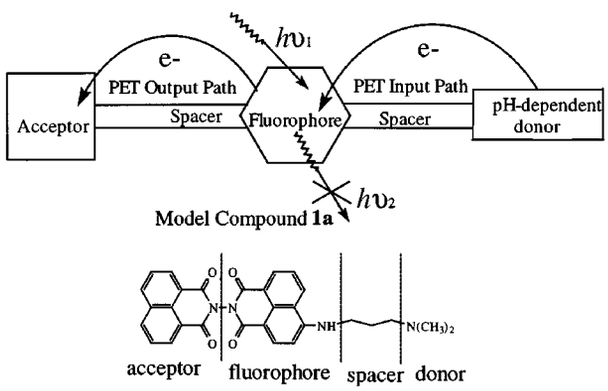


Fig. 1 Schematic representation of the input and output photo-induced electron transfer paths in the PET model compound **1a**. PET occurs from donor to fluorophores, *i.e. via* the PET input path, or from the fluorophore to the acceptor, *i.e. via* the PET output path. The PET input path can be switched off through protonation of the tertiary amine donor, and the PET output path can be shut down through modifying the structure of the acceptor into the same as that of the donor. The PET process occurring *via* either PET path can quench the fluorescence from the fluorophore. Only if both the input and output paths are switched off, can fluorescence from the fluorophore recover.

On consideration of the above aspects, we synthesized model compound **1a** according to the following PET model (see Fig. 1). Its PET behavior could be illustrated by reference compounds **2a**, **1b**, **2b**, **1c** in Scheme 1.

In model compound **1a**, the tertiary amine acts as the electron donor, the 4-amino-1,8-naphthalimide is the fluorophore, the non-substituted 1,8-naphthalimide is the electron acceptor and the covalent hydrocarbon chain is the electron transfer spacer. The PET input path is from the nitrogen atom of the tertiary amine to the 4-amino-1,8-naphthalimide fluorophore *via* the covalent hydrocarbon chain spacer.[10] The PET output path is from the 4-amino-1,8-naphthalimide fluorophore to the

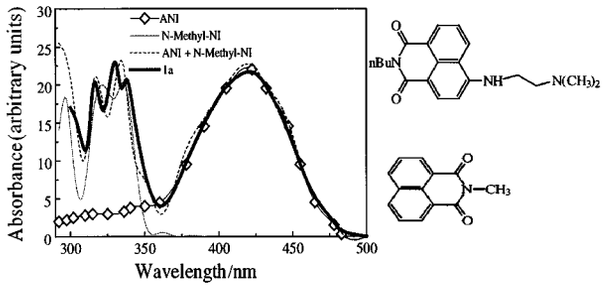
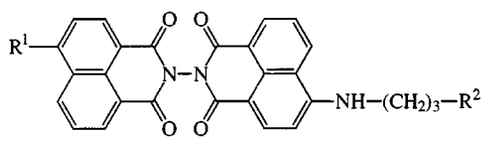


Fig. 2 The absorption spectrum of **1a** and the reference spectra for its respective components *N*-methyl-NI and ANI (in THF) as well as the sum of the absorption spectra of ANI and *N*-methyl-NI.



Compound	$-R^1$	$-R^2$
1a	–H	$-N(CH_3)_2$
2a	$-NH(CH_2)_3R^2$	$-N(CH_3)_2$
1b	–H	$-N^+(CH_3)_3I^-$
2b	$-NH(CH_2)_3R^2$	$-N^+(CH_3)_3I^-$
1c	–H	$-CH_3$

Scheme 1 The chemical structures of the model compound **1a** and its reference compounds used in this study.

non-substituted 1,8-naphthalimide *via* the N–N bond.[11] The PET input path is controlled by protonation and the PET output path can be governed by the photo-induced intramolecular electric field resulting from the asymmetry of the molecule.[10]

It is well known that photo-induced electron transfer from the nitrogen atom of the tertiary amine donor to the 4-amino-1,8-naphthalimide fluorophore quenches the fluorescence of 4-amino-1,8-naphthalimide.[10] The intramolecular energy transfer from 4-amino-1,8-naphthalimide to the non-substituted 1,8-naphthalimide is not energetically feasible because the singlet excited state of 4-amino-1,8-naphthalimide is lower than that of the non-substituted 1,8-naphthalimide. Therefore, the fluorescence quenching of 4-amino-1,8-naphthalimide must result from PET instead of energy transfer. On the other hand, depending on the transient absorption spectral data, Wasielewski's group has discovered that the attachment of one or two electron acceptors, *e.g.* 1,8:4,5-naphthalic diimide or pyromellitic diimide or both, to the 4-amino-1,8-naphthalimide fluorophore, will quench the fluorescence, too.[13] Such an observation is ascribed to the fact that the emission process competes with the forward electron transfer from the fluorophore, *i.e.*, 4-amino-1,8-naphthalimide, to the additional non-substituted naphthalimide acceptor.[13] In our model system, such fluorescent quenching due to the ET from the 4-amino-1,8-naphthalimide donor to the non-substituted 1,8-naphthalimide acceptor is also observed. Therefore, fluorescence quenching of the fluorophore 4-amino-1,8-naphthalimide is a signal for the occurrence of the PET process in the naphthalimide-based compounds of this paper.

Results and discussion

The ground state absorption spectrum of model compound **1a** can be reconstructed from the sum spectra of appropriate reference compounds for its respective components (see Fig. 2). The fact that the absorption spectrum of model compound **1a** can be reconstructed from respective reference compounds of its components indicates that the electronic coupling between the fluorophore 4-amino-1,8-naphthalimide and the acceptor non-substituted 1,8-naphthalimide is weak, which favors electron transfer from the fluorophore to the acceptor.[13] The dihedral

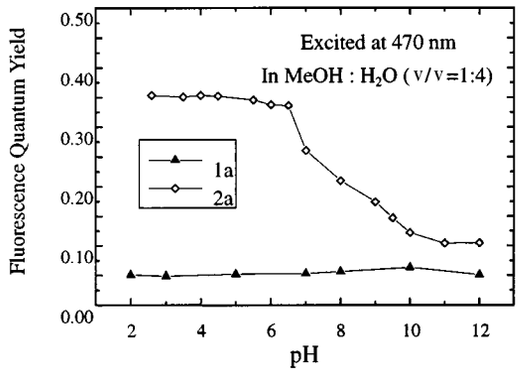


Fig. 3 Fluorescence quantum yield φ_F *versus* pH for **1a** and reference compound **2a**.

angle of the two naphthalimides is calculated to be 90° (MMplus, Hyperchem). These data suggest that steric hindrance due to the four carbonyl groups prevents the conjugation of the two naphthalimides and thus guarantees electronic insulation between the two components. In some similar structures, ET *via* the N–N bond between naphthalimide and pyromellitimide has also been proved.[5,16]

For PET model compound **1a**, ET from the tertiary amine donor to the non-substituted naphthalimide acceptor occurs only if both the input and output PET paths are of the status of "on". Therefore, the fluorescence of the 4-amino-1,8-naphthalimide fluorophore is always quenched if the two paths keep in "on" status. Furthermore, even if the PET input path is shut down through protonation of the tertiary amine, forward electron transfer will still occur from the excited singlet state of 4-amino-1,8-naphthalimide to the non-substituted 1,8-naphthalimide acceptor and quenches the fluorescence of 4-amino-1,8-naphthalimide. Thus, the fluorescence of **1a** does not vary obviously with pH value. However, if a completely identical amine is introduced at the 4-position on the non-substituted 1,8-naphthalimide, *i.e.*, reference compound **2a**, the plot of φ_F *vs.* pH is typically characteristic of a pH-probe. For reference compound **2a**, recovery of the fluorescence of 4-amino-1,8-naphthalimide is apparent when the tertiary amine is protonated, similar to the phenomenon observed in the reported PET model compound *N*-alkylated-4-(*N*,*N*-dialkylated)ethanediamine.[10] The above result is shown in Fig. 3 and Table 1.

Due to the symmetric configuration of **2a**, the dipole moment between two naphthalimide moieties in the excited state is destroyed. Hence, the intramolecular electric field between the two naphthalimide moieties disappears and the output PET path is switched off. [20,21] That is to say, in **2a**, there is no electron transfer through the N–N bond, which links the two identical naphthalimide moieties. When the PET input path is shut down by protonation of the tertiary amine, the fluorescence will recover. So, the plot of φ_F *vs.* pH for **2a** is characteristically pH-dependent. In conclusion, the fluorescence of the 4-aminonaphthalimide fluorophore recovers only if both the input and output PET paths are switched off.

To confirm the above discussion, we prepared reference compounds **1b** and **2b**, in which the tertiary amines are quaternized. The input PET path is locked in the status of "off" by the quaternization of the tertiary amine donor. In this case, the fluorescence of **1b** and **2b** is intrinsically characteristic for pH-independence, which is shown in Fig. 4. However, it is worth noting that the fluorescence of **1b** is still quenched, while the fluorescence of **2b** is apparent. Such remarkably different fluorescence behavior is ascribed to the "on" and "off" status of the PET output path in **1b** and **2b**, respectively. In compound **1b**, PET still occurs from the fluorophore, *i.e.*, the 4-amino-1,8-naphthalimide (which acts as a donor at this time), to the electron acceptor, *i.e.*, the non-substituted 1,8-naphthalimide, and causes the fluorescence to be quenched. But PET stops in

Table 1 Absorption and fluorescence spectral data of **1a**, **2a**, **1b** and **2b**

Compounds	**1a**	**2a**	**1b**	**2b**	**1c**
λ_{Abs}^{max}/nm (acid)	442.6	458.1	448.2	470.0	
λ_{Abs}^{max}/nm (base)	455.3	462.4	452.4	472.3	
λ_{Em}^{max}/nm (acid, excited at 470 nm)	544.2	545.2	545.5	549.0	
λ_{Em}^{max}/nm (base, excited at 470 nm)	548.8	594.8	557.3	572.0	
φ_F(acid)	0.05	0.35	0.05	0.34	
φ_F(base)	0.05	0.1	0.05	0.34	
FE = φ_F(acid)/φ_F(base)	1	3.5	1	1	
(Factor for proton-induced fluorescence enhancement)					
φ_F in ethanol (excited at λ_{Abs}^{max})	0.16 (442.6 nm)	0.59 (453.4 nm)			0.20 (443.5 nm)
φ_F in water			0.029	0.34	
φ_F in ethanol : water (v/v = 1 : 1)			0.079	0.51	

The profiles of fluorescence quantum yield φ_F *vs.* pH for **1a**, **1b**, **2a**, **2b** are performed on excitation at 470 nm with the concentration of 10^{-5} M in aerated methanol : water (1 : 4, v/v). Rhodamine B is employed as an internal standard and its fluorescence quantum yield is defined as $\varphi_{F(RhB)}$ = 1 (excited at 470 nm). Fluorescence quantum yields are calculated using the relationship: $\varphi_F = \varphi_{F(RhB)}(A_{RhB}/A)(I/I_{RhB})$, where A_{RhB}/A represents the ratio of the absorbance of Rhodamine B in aerated methanol : water (1 : 4, v/v) at 470 nm to that of sample in the measured solvent, and I/I_{RhB} is the ratio of the integral fluorescent peak area of sample (excited at 470 nm, if not noted otherwise) to that of Rhodamine B on excitation at 470 nm in aerated methanol : water (1 : 4, v/v). No hydrolysis of the naphthalimide ring occurs under the experimental conditions (pH = 2.5–12).

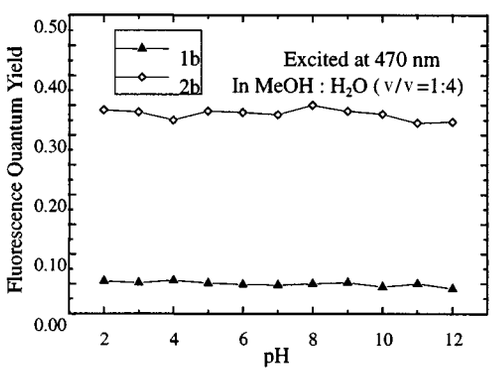


Fig. 4 Fluorescence quantum yield φ_F *versus* pH for reference compounds **1b** and **2b**.

compound **2b**, because the intramolecular electric field between the two identical naphthalimide moieties is destroyed in such a symmetric chemical structure as reference compound **2a**.

Reference compound **1c** was prepared to confirm the fact that PET still occurs between the fluorophore, *i.e.*, 4-amino-1,8-naphthalimide, and the acceptor, *i.e.*, non-substituted 1,8-naphthalimide, even if the electron input path is suppressed by the protonation of tertiary amine, that is to say, without the donor, the PET between the 4-amino-1,8-naphthalimide fluorophore and the non-substituted 1,8-naphthalimide acceptor is still a thermodynamically feasible process. In reference compound **1c**, there is no tertiary amine on the side chain, and the PET process from donor to fluorophore no longer takes place. For reference compound **1c**, the free energy ΔG_{CS} for charge separation from the excited singlet state of 4-(butylamino)-1,8-naphthalimide to the non-substituted 1,8-naphthalimide acceptor can be calculated using eqn. (1),[22] where E_{Ox} is the

$$\Delta G_{CS} = E_{Ox} - E_{Red} - \frac{e_0^2}{\varepsilon_s r_{12}} - E_s \qquad (1)$$

oxidation potential energy of the donor, E_{Red} is the reduction potential energy of the acceptor, E_s is the potential energy of the first excited singlet state of the donor, e_0 is the charge of an electron, ε_s is the static dielectric constant of the solvent, and r_{12} is the center-to-center distance between the donor and the acceptor. E_{Ox} of 4-(alkylamino)-1,8-naphthalimide is 1.1 eV *vs.* SCE,[22] E_{Red} of the non-substituted 1,8-naphthalimide is −1.23 eV *vs.* SCE,[23] ε_s is 2.24 for toluene,[24] and from a structures calculation using the MMplus method (Hyperchem) r_{12} is estimated to be 11 A°. E_s of 4-(alkylamino)-1,8-naphthalimide is ~2.8 eV in toluene.[5,13,22] The free energy of electron transfer ΔG_{CS} is calculated to be −1.12 eV (25.7 kcal mol^{-1}). The sufficiently negative value of ΔG_{CS} shows that for reference compound **1c**, the PET process between the amino-substituted naphthalimide and the non-substituted naphthalimide is thermodynamically feasible. The fluorescence lifetime τ_F of **1c** is measured to be 13.5 ns, longer than the reported τ_F (10.5 ns)[25] of mono *N*-butyl-4-(butylamino)-1,8-naphthalimide. The prolongation of the excited state in **1c** may be ascribed to the additional PET process from 4-(butylamino)-1,8-naphthalimide to the non-substituted 1,8-naphthalimide, which otherwise does not occur in the monomer *N*-butyl-4-(butylamino)-1,8-naphthalimide.[5,13]

On the other hand, the PET process is largely influenced by the polarity of solvents, because PET is considerably accelerated in polar media for 4-amino-1,8-naphthalimides and fluorescence will be diminished in a solvent with high polarity.[10] The φ_F of **1a**, **2a**, **1b** and **1c**, is much poorer in the highly polar solvent EtOH than that measured in the low polar solvent THF, due to the occurrence of PET in these compounds. But comparably, the φ_F of reference compound **2b** remains steady *versus* the solvent polarity, since both the input and output electron path are switched off in **2b** as discussed previously. Eqn. (2)

$$\bar{\nu} = -\frac{2\mu_e^2}{hca^3}\left[\frac{\varepsilon_s - 1}{2\varepsilon_s + 1} - \frac{n^2 - 1}{4n^2 + 2}\right] \qquad (2)$$

can be employed to estimate the molecular dipole moment in the electron transfer (ET) state of PET model compound **1a** if the ET emission maximum is obtained in different solvents,[13,26–28] where h is Planck's constant, c is the speed of light, n is the refractive index of the medium, ε_s is the static dielectric constant of the solvent, μ_e is the dipole moment of the ET state, and a is the semimajor axis of an ellipsoidal cavity containing **1a**.

The value of the dipole moment of the ET state is determined from the slope of the plot (Fig. 5) of the solvatochromic shift of the ET emission maximum. For a = 10 Å (the value is based on the a (5 Å) of mono-1,8-naphthalimides, *e.g.* *N*-phenyl-4-amino-1,8-naphthalimide, which are half the size of bis-1,8-naphthalimides),[13] μ_e = 26.3 D.

Compared with the previous assessment of 11 D for the excited state dipole moment μ_e in *N*-alkylated-4-amino-1,8-naphthalimide,[10,13] the relative increase of μ_e in bis-1,8-naphthalimide is ascribed to the introduction of another electron acceptor, *i.e.*, the non-substituted 1,8-naphthalimide.[29] This fact shows that the non-substituted 1,8-naphthalimide acts exactly as an acceptor to influence the PET process, and PET can occur between the two different naphthalimide moieties *via* the N–N bond.

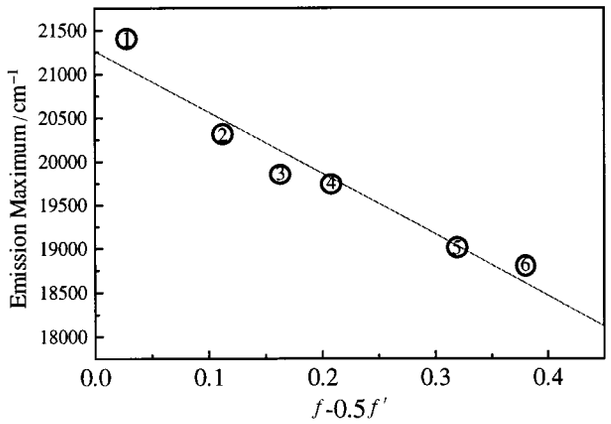


Fig. 5 Plot of the fluorescence emission maximum of **1a** as a function of the solvent polarity factor as given in eqn. (2), where $f = (\varepsilon_s - 1)/(2\varepsilon_s + 1)$ and $f' = (n^2 - 1)/(2n^2 + 1)$. The following solvents were used: 1: hexane, 2: toluene, 3: tetrahydrofuran, 4: chloroform, 5: dichloromethane, 6: ethanol. The static dielectric constant ε_s and refractive index n were obtained from ref. 24. All the measurements were performed at 20 °C.

Experimental

UV–visible and fluorescence spectra were recorded with Shimadzu UV-260 and HITACHI-850 instruments, respectively. The nanosecond time-resolved fluorescence decay kinetics were measured with a fast-response diode (DET2-Si, Thorlabs Inc.), which connected with a digital storage oscilloscope (Tektronix TDS 420). The excitation light was from a nitrogen gas laser, 337 nm with a 6–7 ns pulse width (Radiant Dyes Laser Acce.). The above measurements were performed in air at room temperature. Proton NMR and mass spectra were obtained with Bruker AM-400 (400 MHz) and HP5989A spectrometers, respectively. Elemental analyses were performed by MOD-1101.

General synthetic method

All the compounds studied were derived from 4-nitro-*N*-(*N*-1,8-naphthalimide)-1,8-naphthalimide (compound **1**) and 4-nitro-*N*-[*N*-(4-nitro-1,8-naphthalimide)]-1,8-naphthalimide (compound **2**), which were prepared through the reaction of 4-nitro-1,8-naphthalic anhydride with *N*-amino-1,8-naphthalimide and *N*-amino-4-nitro-1,8-naphthalimide, respectively in absolute ethanol for about 8 h.

Compounds **1a** and **2a** were obtained from the interaction of *N*,*N*-dimethylpropane-1,3-diamine with compound **1** and compound **2**, respectively in DMF at 110 °C for 1.5 h. Pure products could be recrystallized from THF. A similar procedure was used to prepare compound **1c**, except that $CHCl_3$ was applied as recrystallization solvent. The synthesis of compounds **1b** and **2b** was performed by the reaction of CH_3I with **1a** and **2a**, respectively in ethanol for 30 min. DMF was used as recrystallization solvent to obtain pure compounds. [25,30–33]

Compound 1

MS (EI, 70 eV): *m*/*z*(%) $[M + 1]^+$ 438(13.3), $[M]^+$ 437(50.6), $[M - NO]^+$ 407(25.84), $[M - NO_2]^+$ 392(10.94), 225(15.62), 195(16.67); ^{1}H-NMR (in DMSO-d$_6$) δ(ppm) 8.93 (d, J = 8.25 Hz, 1H), 8.83 (m, J = 8.25 Hz, J = 7.06 Hz, 2H), 8.25 (t, J = 7.08 Hz, J = 8.10 Hz), 8.05 (t, 2H), 8.70 (m, 5H); Anal. Calc. for $C_{24}H_{11}N_3O_6$: C, 65.90; H, 2.52; N, 9.61. Found: C, 65.69; H, 2.50; N, 9.46%.

Compound 2

MS (EI, 70 eV): *m*/*z* (%) $[M]^+$ 482(100), $[M - NO]^+$ 452(17.14), $[M - 2NO + 1]^+$ 423(19.72), 225(59.23), 179(39.05); ^{1}H-NMR (in DMSO-d$_6$) δ(ppm) 8.25 (t, J = 8.19 Hz, J = 8.02 Hz, 2H), 8.67 (d, J = 8.03 Hz, 2H), 8.83 (m, 4H), 8.90 (d, J = 8.75 Hz, 2H); Anal. Calc. for $C_{24}H_{10}N_4O_8$: C, 59.75; H, 2.07; N, 11.62. Found: C, 59.99; H, 2.17; N, 11.57%.

Compound 1a

MS (EI, 70 eV): *m*/*z*(%) $[M]^+$ 492(4.69), $[M - 1]^+$ 491(11.39), $[M - CH_2N(CH_3)_2]^+$ 434(48.81), $[M - CH_2CH_2N(CH_3)_2]^+$ 420(35.27); ^{1}H-NMR (in DMSO-d$_6$) δ(ppm) 6.90 (d, J = 8.79 Hz, 1H), 8.40 (d, J = 8.77 Hz, 1H), 7.80 (t, J = 7.51 Hz, J = 8.42 Hz, 1H), 8.61 (d, J = 7.53 Hz, 1H), 8.85 (d, J = 8.44 Hz, 1H), 8.70 (m, 4H), 8.00 (t, J = 7.78 Hz, J = 7.81 Hz, 2H), 2.25 ($N(CH_3)_2$, s, 6H), 2.38 (–CH_2–$N(CH_3)_2$, t, 2H), 3.50 (NH–CH_2–, t, 2H), 1.85 (NH–CH_2–CH_2, m, 2H).

Compound 2a

^{1}H-NMR (in DMSO-d$_6$) δ(ppm) 6.90 (d, J = 8.61 Hz, 2H), 8.32 (d, J = 8.59 Hz, 2H), 7.82 (t, J = 7.51 Hz, J = 8.41 Hz, 2H), 8.61 (d, J = 7.46 Hz, 2H), 8.80 (d, J = 8.44 Hz, 2H), 2.20 ($N(CH_3)_2$, s, 12H), 2.38 (–CH_2–$N(CH_3)_2$, t, 4H), 3.50 (NH–CH_2–, t, 4H), 1.88 (NH–CH_2–CH_2, m, 4H).

Compound 1b

^{1}H-NMR (in DMSO-d$_6$) δ(ppm) 6.90 (d, J = 8.79 Hz, 1H), 8.32 (d, J = 8.77 Hz, 1H), 7.80 (t, J = 7.51 Hz, J = 8.42 Hz, 1H), 8.54 (d, J = 7.53 Hz, 1H), 8.85 (d, J = 8.44 Hz, 1H), 8.70 (m, 4H), 8.00 (t, J = 7.78 Hz, J = 7.81 Hz, 2H), 3.12 ($N^+(CH_3)_3$, s, 9H), 3.40 (–CH_2–$N^+(CH_3)_3$, t, 2H), 3.63 (NH–CH_2–, t, 2H), 2.15 (NH–CH_2–CH_2, m, 2H).

Compound 2b

^{1}H-NMR (in DMSO-d$_6$) δ(ppm) 6.90 (d, J = 8.61 Hz, 2H), 8.35 (d, J = 8.59 Hz, 2H), 7.80 (t, J = 7.51 Hz, J = 8.41 Hz, 2H), 8.60 (d, J = 7.46 Hz, 2H), 8.85 (d, J = 8.44 Hz, 2H), 3.10 ($N^+(CH_3)_3$, s, 18H), 3.40 (–CH_2–$N(CH_3)_3$, t, 4H), 3.60 (NH–CH_2–, t, 4H), 2.20 (NH–CH_2–CH_2, m, 4H).

Compound 1c

MS (EI, 70 eV): *m*/*z*(%) $[M + 1]^+$ 464 (22.62), $[M]^+$ 463(62.50), $[M - CH_2CH_2CH_3]^+$ 420(100), 223(13.94), 195(14.12), 182(78.30); ^{1}H-NMR (in DMSO-d$_6$) δ(ppm) 6.90 (d, J = 8.96 Hz, 1H), 8.38 (d, J = 8.97 Hz, 1H), 7.80 (t, J = 7.60 Hz, J = 8.20 Hz, 1H), 8.56 (d, J = 7.57 Hz, J = 0.70 Hz, 1H), 8.88 (d, J = 8.20 Hz, J = 0.70 Hz, 1H), 8.63 (m, 4H), 8.00 (t, J = 7.62 Hz, J = 7.98 Hz, 2H), 0.9 (–CH_3, t, 3H), 1.45 (CH_2–CH_3, m, 2H), 3.50 (NH–CH_2–, m, 2H), 1.73 (NH–CH_2–CH_2, m, 2H); Anal. Calc. for $C_{28}H_{21}O_4N_3$: C, 72.57; H, 4.54; N, 9.07. Found: C, 72.52; H, 4.56; N, 9.21%.

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