Synthesis of Diazacrown Ethers with Chromophores and Their Photoinduced Charge-Separation with Methyl Viologen

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Two 4,13-diaza-18-crown-6 ethers with either two pyrenyl or two carbazolyl groups were synthesized. The two crown ethers can form complexes with methyl viologen in methanol solution. Photoirradiation of the complexes resulted in the electron transfer from the excited states of the chromophores to methyl viologen as demonstrated by the quenching of the chromophore fluorescence and the detection of the absorption spectrum of the generated viologen radical cation. The back electron transfer in these systems was inhibited by the electrostatic repulsion between the positively charged viologen radical cation and the generated chromophore radical cation. Long-lived charge separation states (up to tens of min) were observed.

Introduction

Photoinduced electron transfer and subsequent charge separation are the principal steps for the photoconversion of solar energy into electric or chemical energy. A key feature in the mechanism of photoconversion is the initial storage of a fraction of light energy in the form of a long-lived charged radical pair.[1] The long lifetime of the charge-separation state directly leads to the high efficiency of the conversion. However, Since the ion pair generated in the forward electron transfer stores a considerable amount of energy, the back electron transfer is thermodynamically allowed and is usually diffusion-controlled in homogeneous solution. In attempt to impede the energy-wasting back electron transfer, many efforts have been performed.[2-14] In the present work, we report the synthesis of diazacrown ethers containing pyrenyl or carbazolyl groups. These crown ethers may complex with methyl viologen. Photoinduced electron transfer within the complexes resulted in the charge separated pair. Due to the electrostatic repulsion between the generated charged counters, back electron transfer was inhibited, and the charge separation state may survive up to tens of minutes.

Results and discussion

Synthesis of diazacrown ethers with pyrenyl or carbazolyl groups

The structures of the compounds we studied and their complexes with methyl viologen (**MV**) are shown in Scheme 1. These compounds were synthesized by two steps: the first step is to synthesize 1,7,10,16-tetraoxo-4,13-diazacyclooctadecane (diaza-18-crown-6) (**C**).[15] Then the crown ether **C** reacts respectively with 3-(4-bromobutoxymethyl)pyrene (**Py-Br**) or N-(10-bromodecyl)carbazole (**Cz-Br**) to give **Py-C** and **Cz-C**. The whole synthetic procedures are shown in Scheme 2.

Complexation of **Py-C**, **Cz-C** with MV^{2+} and photoinduced charge separation

It has been well established[16-18] that the macrocyclic

crown ether can complex with MV^{2+}. To ascertain the formation of the complexes of **Py-C** and **Cz-C** with MV^{2+}, the fluorescence spectra of **Py-C**, **Cz-C** and their model compounds (1-methoxybutyl)pyrene-3 (**Py**) and N-decylcarbazole (**Cz**) in solution in the presence of MV^{2+} and the absorption spectra of the viologen radical $MV^{+\cdot}$ generated by electron transfer were examined. **Cz** in methanol solution shows structural fluorescence in the range of 340—410 nm with maxima at 352 and 368 nm, and a shoulder at 388 nm (excited at 295 nm, Fig. 1).
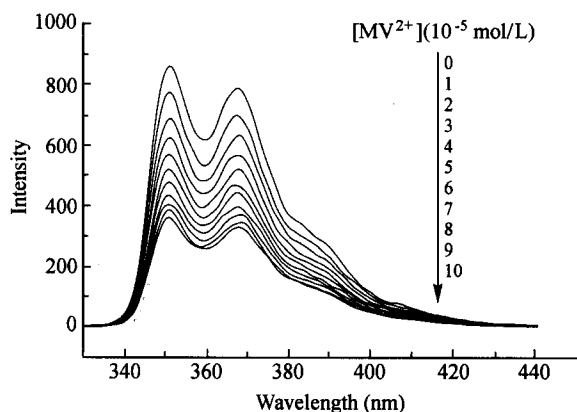

Fig. 1 Fluorescence spectra of **Cz** in MeOH solution ($\lambda_{ex} = 295$ nm) as a function of MV^{2+} concentration.

This emission is quenched by MV^{2+} according to the Stern-Volmer dependence. The quenching constant was determined to be *ca.* $1.02 \times 10^{12}(mol/L)^{-1} \cdot s^{-1}$ by taking that the fluorescence lifetime of **Cz** in the absence of MV^{2+} is *ca.* 13.9 ns. The quenching constant is about one hundred times of the encounter constant limit in solution, which is probably due to the formation of the complex between carbazole and methyl viologen. The energy of the singlet excited state of **Cz** is lower than that of MV^{2+} as estimated from their absorption spectra. Thus, the possibility of singlet-singlet energy transfer responsible for the fluorescence quenching is excluded. Therefore, we examined the reality of electron transfer between the two chromophores as the cause of the fluorescence quenching. The free energy change (ΔG) involved in a photostimulated electron transfer process can be estimated by Rehn-Weller equation:[19,20]

$$\Delta G = E_{ox}(D) - E_{red}(A) - \Delta E_{00} - e^2/\varepsilon a \quad (1)$$

Where ΔE_{00} is the excited state energy, and in this case

represents the singlet excited state energy of **Cz** (*ca.* 348.3 kJ/mol).[21] $E_{ox}(D)$ and $E_{red}(A)$ are the redox potentials of the donor and the acceptor respectively, and in this case the oxidation potential of **Cz** is *ca.* 1.10 V *vs.* SCE[21] and the reduction potential of MV^{2+} is -0.44 V *vs.* SCE.[22] $e^2/\varepsilon a$ is the Coulombic interaction in the ion pair state whose magnitude depends on the distance (a) between the donor and the acceptor and on the dielectric constant (ε) of the medium separating the charges.[19,20] For a contact ion pair in acetonitrile, this term is estimated to be *ca.* -0.05 V, and generally shows a minor impact on ΔG. Calculation according to Eq. (1) reveals that electron transfer from the singlet excited state of **Cz** to MV^{2+} is exothermic by *ca.* -194.6 kJ/mol. Thus, we attributed the fluorescence quenching to the electron transfer from the excited state of **Cz** to MV^{2+}. This conclusion is supported by the observation of the absorption spectra of the generated viologen radical $MV^{+\cdot}$. Irradiation of the degassed solution of **Cz** in methanol in the presence of MV^{2+} in high concentration readily results in the absorption of $MV^{+\cdot}$ in two bands with λ_{max} at *ca.* 396 and 600 nm. However, at the concentration of MV^{2+} below 5×10^{-6} mol/L, no $MV^{+\cdot}$ absorption was obtained even if the irradiation lasts a long period. Evidently in such dilute solution, the intermolecular quenching of excited **Cz** by MV^{2+} is negligible.
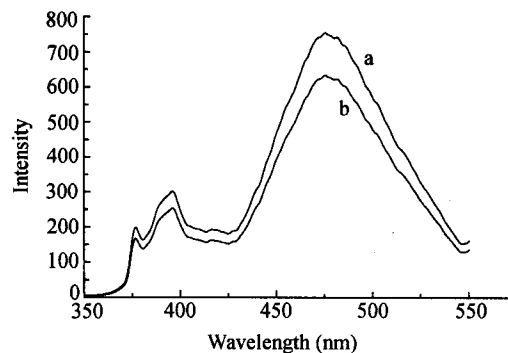
In contrast to **Cz**, even in dilute MV^{2+} solution, the fluorescence of **Cz-C** is significantly quenched by MV^{2+}. The fluorescence efficiency of the **Cz-C** in the presence of 5×10^{-6} mol/L MV^{2+} is *ca.* 16% less than that in the absence of MV^{2+}. At the concentration of MV^{2+} below 5×10^{-6} mol/L, the quenching efficiency is kept constant. The fluorescence lifetimes of **Cz-C** in the presence of 5×10^{-6} mol/L MV^{2+} and in the absence of MV^{2+} were determined to be 10.5 and 12.9 ns, respectively. These data allow the calculation of the quenching constant and the quantum yield of the quenching, which were obtained to be 1.7×10^7 s^{-1} and 18.6%, respectively. The value of the quenching efficiency thus obtained is comparable with that from the fluorescence efficiency measurements. Irradiation of **Cz-C** solution in methanol in the presence of 5×10^{-6} mol/L MV^{2+} does lead to the formation of $MV^{+\cdot}$. Fig. 2 shows the absorption spectra of $MV^{+\cdot}$ radical[23] for irradiation of a **Cz-C** solution in the presence of the 5×10^{-6} mol/L MV^{2+} with a 450 W Hadovia lamp as a function of irradiation
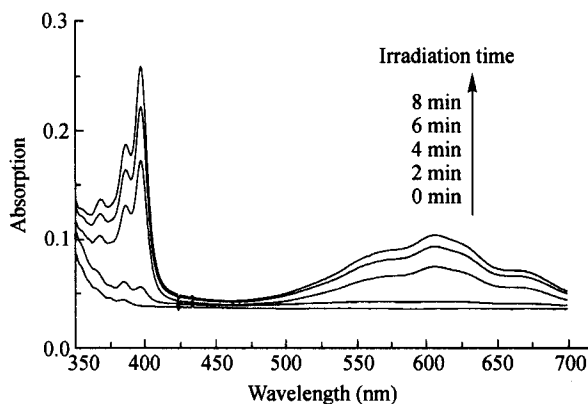
Fig. 2 Absorption spectra of $MV^{+\cdot}$ radical as a function of
        irradiation time for **Cz-C** (5×10^{-6} mol/L) solution
        in methanol in the presence of 5×10^{-6} mol/L MV^{2+}.

Fig. 3 Fluorescence spectra of **Py-C** in MeOH solution (λ_{ex}
        $= 345$ nm) in the absence of MV^{2+} (a) and in the
        presence of 5×10^{-6} mol/L MV^{2+} (b).

time. The spectra clearly document the continuous growth of $MV^{+\cdot}$ radical. We proposed that a complex ($Cz-MV^{2+}$ in Scheme 1) was formed between **Cz-C** and MV^{2+}. On the basis of the size of MV^{2+} molecule and the cavity of the crown ether as reported in the literatures,[16-18] formation of a 1:1 host-guest complex is most possible. Thus, the donor and the acceptor in $Cz-MV^{2+}$ are tethered by an alkyl chain, and the electron transfer is intramolecular. For samples thoroughly deoxygenated and kept in an anaerobic atmosphere, the charge-separation state may survive up to tens of minutes. The long lifetime of the charge-separated state probably originates from the electrostatic repulsion between the positively charged viologen radical ($MV^{+\cdot}$) and the positively charged carbazolyl radical generated by the forward electron transfer in $Cz-MV^{2+}$. Thus, it is difficult for $MV^{+\cdot}$ and $Cz^{+\cdot}$ to approach each other and the back electron transfer is inhibited. The enhancement of charge separation due to electrostatic repulsion has been well established with other systems.[11,24-27]

Qualitatively similar results were obtained for complexation between **Py-C** and MV^{2+} in methanol solution. **Py-C** shows both monomer and excimer fluorescence, and even at very low concentration the excimer fluorescence dominates the fluorescence spectrum (Fig. 3). The reason for preferable formation of excimer is that the two pyrenyl groups in **Py-C** are connected to one crown ether macrocycle, thus are in close proximity to each other. Both the monomer and the excimer fluorescence can be quenched by MV^{2+}. We believe that the quenching is due to electron transfer from the excited

pyrenyl to MV^{2+}, since the calculated ΔG involved in this electron transfer process according to Eq. (1) is exothermic by *ca*. -159.1 kJ/mol, taking that the energy of the pyrenyl singlet excited state is 322.3 kJ/mol,[28] and the oxidation potential of pyrenyl is *ca*. 1.20 V vs. SCE.[28] At MV^{2+} concentration below 5×10^{-6} mol/L the fluorescence quenching is significant and independent on MV^{2+} concentration. The quenching efficiency and quenching constant were calculated to be *ca*. 16.8% and *ca*. 9.0×10^{5} s^{-1} respectively from the monomer fluorescence lifetimes of **Py-C** in the presence of 5×10^{-6} mol/L MV^{2+} (*ca*. 187 ns) and in the absence of MV^{2+} (*ca*. 225 ns). Irradiation of **Py-C** solution in the presence of MV^{2+} in low concentration results in $MV^{+\cdot}$ radical as detected by absorption spectra. All these observations suggest that **Py-C** forms $Py-MV^{2+}$ (Scheme 1), a 1:1 complex with MV^{2+}, and the fluorescence quenching is intramolecular in dilute solution of MV^{2+}.

Conclusion

Novel diazacrown ethers with two carbazolyl (**Cz-C**) or two pyrenyl (**Py-C**) groups were synthesized for the first time. The compounds can form 1:1 host-guess complexes with methyl viologen. The complexes have the general electron donor-acceptor (D-A) diad structure. The fluorescence quenching of the carbazyl and pyrenyl chromophores in solution by MV^{2+} and the detection of absorption spectrum of viologen radical after irradiation of the complexes demonstrated that photoinduced "intramolecular" electron transfer and the subsequent charge separation take place within the complexes. Back electron

Scheme 1
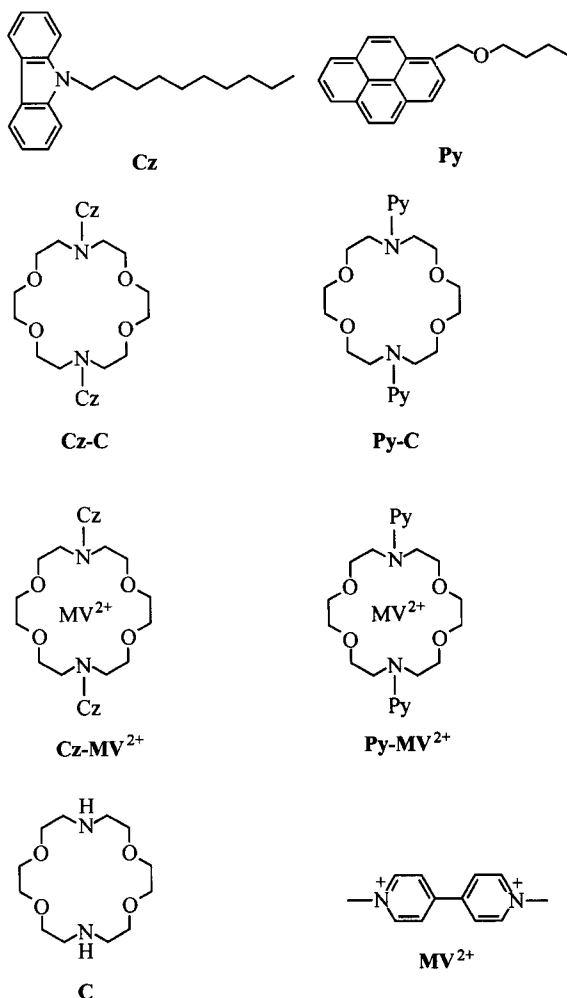
transfer was retarded due to the electrostatic repulsion between the generated positively charged chromophore radical and viologen radical. The charge separated states may survive up to tens of minutes.

Experimental

Apparatus and materials

IR spectra were recorded on a PE Spectrum BX FT-IR System spectrometer. ^{1}H NMR spectra were measured on a Bruker DPX-400 spectrometer with TMS as an internal standard. Mass spectra were obtained on a VG ZAB-HS (UK) organic mass spectrometer. Element analyses were performed on a HERAUS CHN-RAPID element analysis spectrometer. UV adsorption spectra were measured on a PE UV/VIS Spectrometer Lambda 20.

Fluorescence spectra were measured on a PE LS 50B luminescence spectrometer. Fluorescence lifetimes were measured by the technique of single-photon counting on a HORIBA NAES-1100 time-resolved spectrofluorometer.

Methyl viologen and pyrene were Aldrich products and used directly without further purification. Methanol was distilled. All other commercially available chemical reagents were used directly without further purification.

Irradiation experiments

A 500 W xenon lamp was used as light resource. Acetone solution was used to filter off the light with $\lambda <$ 330 nm. Methanol solution was deoxygenated thoroughly by pure argon gas.

Preparation of 1, 7, 10, 16-tetraoxo-4, 13-diaza-18-crown-6 (C)

This crown ether was prepared and identified according to the methods reported in the literatures.[15,29]

Preparation of N-(10-bromodecyl) carbazole (Cz-Br)

Cz-Br was prepared by a modified method of N-alkylation of carbazole in the presence of a quarternary ammonium salts as phase transfer catalysts.[30] To a mixture of carbazole (1.0 g, 6.0 mmol), benzene (3 mL), benzyltrimethylammonium chloride (BTMAC) (50 mg) and 50% aqueous sodium hydroxide (3 mL), excess amount (tenfold equivalent to carbazole) of 1,10-dibromodecane was added. Stirring was continued at 50—60℃ for 4 h. The benzene was evaporated and the residue was extracted with chloroform. The organic layer was washed with water, dried with anhydrous sodium sulphate and evaporated to remove the chloroform. A brown residue was obtained. The excess dibromide could not be easily distilled under reduced pressure as described in literature[31] due to its high boiling points. Pale yellow crystalline products were obtained when the residue was treated by silica gel column with petroleum as eluent. Further recrystalization in petroleum gave a white product, yield: 85%. m.p. 30℃; IR (KBr) ν: 3053, 2923, 2854, 1596, 1485, 1455, 1325, 1226, 1150, 746, 723 (C—Br) and 560 cm^{-1}; ^{1}H NMR (CDCl$_3$)δ:1.10—1.50(m,12H),1.80—2.0(m,

Scheme 2
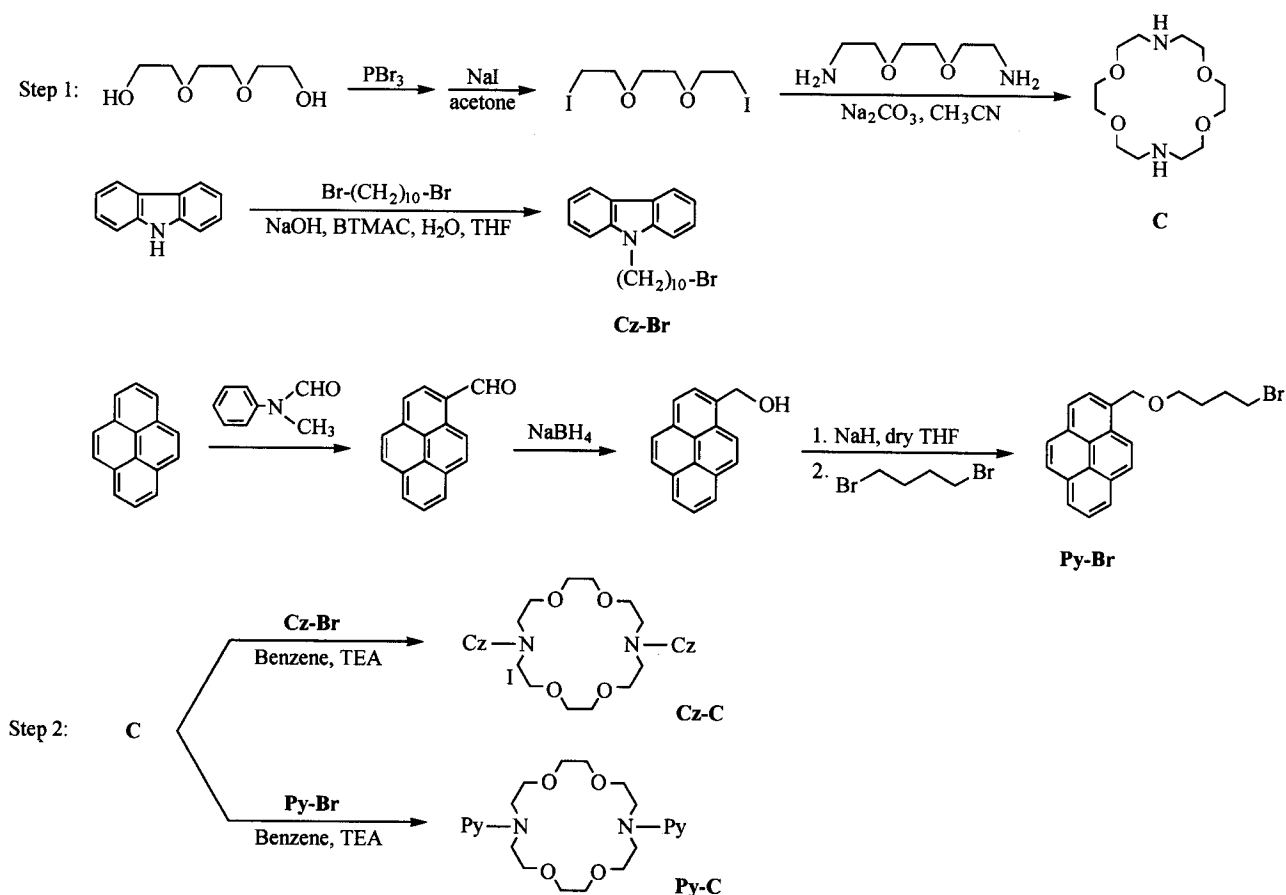
4H), 3.4 (t, $J = 8$ Hz, 2H), 4.4 (t, $J = 8$ Hz, 2H), 7.2—7.35 (m, 2H), 7.4—7.6 (m, 4H), 8.10—8.23 (m, 2 H).

Preparation of 3-(4-bromobutoxymethyl)pyrene (**Py-Br**)

Pyrene was formolated according to the literature method[32] and further reduced by $NaBH_4$ to give 3-hydroxymethyl-pyrene. A solution of 0.348 g (1.5 mmol) 3-hydroxymethyl-pyrene, 0.108 g (4.5 mmol) sodium hydride, and 10 mL dry THF was stirred under refluxing in the atmosphere of nitrogen for 4 h. To the resulted semisolid residue (pyrenylmethanol sodium) was added 1.818 g (9 mmol) 1,4-dibromobutane and the solution was continued to be stirred overnight. The residue was filtered and the filtrate after concentrated was treated by silica gel column (petroleum ether as eluent) to give a pale yellow crystal, yield 40%. m.p. 62—64℃. IR (KBr) ν: 3036, 2941, 2854, 1588, 1552, 1479,

1457, 1373, 1341, 1199, 1122, 1093, 845, 755, and 703 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.80—1.82 (m, 2H), 1.96—1.97 (m, 2H), 3.4 (t, $J = 6.6$ Hz, 2H), 3.6 (t, $J = 6.1$ Hz, 2H), 5.23 (s, 2H), 8.01—8.40 (m, 9H); MS (70 eV) m/z (%): 368 ([M + 1]$^+$, 22).

General procedure[33] *for synthesis of N, N'-bis* (10-(9-*carbazyl*) *decyl*)-1,7,10,16-*tetraoxo*-4,13-*diaza*-18-*crown*-6 (**Cz-C**) *and N, N'-bis* (3-*pyrenylmethoxybutyl*)-1,7,10,16-*tetraoxo*-4,13-*diaza*-18-*crown*-6 (**Py-C**)

A solution of 0.5 g **C**, 0.5 g TEA, and twofold equivalent (to **C**) of **Cz-Br** or **Py-Br** in 15 mL benzene was stirred and refluxed under nitrogen overnight. After the white precipitate was filtered, the filtrate was concentrated to about 5 mL and was then transferred into a short silica gel column. Benzene was used to wash down the excess bromides first. A mixed solvent of acetone

and triethylamine (TEA) (95:5 in vol.) was then explored to elute the desired compounds. Recrystallization in alcohol with little chloroform yielded pure products.

Cz-C   White powder, yield: 42%; m. p. 82—84℃; IR (KBr) ν: 3045, 2931, 2854, 1626, 1596, 1459, 1348, 1325, 1245, 1120, 1062, 746 and 720 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ: 1.2—1.5 (m, 24H), 1.62.0 (m, 8H), 3.1—4.0 (m, 28H), 4.3 (t, J = 6.2 Hz, 4H), 7.1—7.3 (m, 4H), 7.3—7.5 (m, 8H), 8.10—8.11 (m, 4H); MS (FAB) m/z (%): 873 ([M + H]$^+$, 64), 449 (5), 361 (8), 335 (10), 194 (18), 180 (100), 168 (21), 100 (23), 55 (52), 44 (48); Anal. calcd for C$_{56}$H$_{80}$N$_4$O$_4$: C 77.06, H 9.17, N 6.42; found C 76.97, H 9.15, N 6.29.

Py-C   Pale yellow crystal, yield 60%; m.p. 106—107℃; IR (KBr) ν: 3036, 2941, 2861, 2802, 1643, 1585, 1475, 1453, 1355, 1300, 1250, 1122, 1090, 842, 755, and 707 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ: 1.6—1.7 (m, 4H), 1.75—1.85 (m, 4H), 2.8—3.3 (m, 24H), 3.4—3.5 (m, 4H), 3.55—3.75 (m, 4H), 5.19 (d, J = 6.3 Hz, 4H), 7.95—8.40 (m, 18H); MS (FAB) m/z (%): 835([M + 1]$^+$, 11), 603 (3), 231 (10), 215(100); Anal. calcd for C$_{54}$H$_{62}$N$_2$O$_6$: C 77.7, H 7.43, N 3.36; found C 77.40, H 7.56, N 3.26.

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