Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for

Study of electron transfer reactions in a dendrimaric assembly: a proper utilization of dendrimer fluorescence

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Experimental section:

Materials and method: Both the generation of dendrimers (G1 and G3), 2,4-dinitrotoluene and HPLC grade methanol were purchased from Sigma-Aldrich and used without further purification. Hydrochloric acid and potassium chloride were purchased from Spectrochem. All the fluorescence quenching experiments have been performed at room temperature (25^0C) and under inert atmosphere. The solutions were allowed to settle for 10 minutes after each addition in the titration experiment to ensure homogeneous mixing.

Steady state absorption and emission spectra were collected by using Perkin-Elmern 750 spectrophotometer and Cary Eclipse fluorescence spectrometer respectively. Time resolved fluorescence data were collected by using a Time correlated single photon counting (Edinburg Instruments, model OB-920) setup. Picosecond pulsed diode lasers of wavelengths 375nm and 405nm were used to excite PAMAM G1 and PAMAM G3 samples respectively. Instrument response function (IRF) was measured by using a scatterer ludox solution and the value of FWHM of the IRF was found to be ~80ps from both the lasers. The lifetime data were analysed by F900 software provided with the TCSPC setup.

Time resolved fluorescence anisotropy was obtained by altering the emission polariser to the parallel and perpendicular directions with respect to the excitation polariser at regular time interval. From the decay of parallel and perpendicular intensity the rotational correlation function r(t) was calculated using the following equation

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \quad \text{.....(S1)}$$

Where $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the time resolved fluorescence intensities at parallel and perpendicular directions. G is the calibration factor for compensating instrumental errors. The rotational time (τ_r) was obtained by fitting the rotational correlation decay with biexponential decay function. The τ_r thus obtained is correlated to the volume of the rotating dipole as explained by Stokes-Einstein-Debye (SED) hydrodynamic theory as follows.

$$\tau_r = \frac{\eta V}{kT} \quad \text{.....(S2)}$$

Where η is the viscosity of the medium, V is the hydrodynamic volume of the rotating sphere, k is the Boltzman constant and T is the temperature.

Cyclic voltammetry experiments were performed in a 25ml electrochemical cell with three electrodes configuration in Metrohm-Autolab insrument. Potentials were recorded with respect to Ag/AgCl electrode in aqueous solution of 0.1 M KCl. Platinum wire electrode and platinum rotating disc working electrode were used for all the measurements. Clear oxidation peaks detected for both the generation of dendrimers.

Changes of thermodynamic parameters for the host-guest complex formation were studied by using MicroCal ITC200 (Malvern Instruments) calorimeter. Heat change at constant temperature (25^0C) during the addition of 1 mM of dendrimer solution to 0.2 mM DNT in methanol (stirring speed of 600 rpm) were recorded and the data was analysed by MicroCal Origin software provided within the instrument.

Tables

Table S1. Rotational anisotropy parameters and hydrodynamic sizes of PAMAM dendrimers:

Dendrimer	τ_1 (a_1)	τ_2 (a_2)	$<\tau>$ (ns)	R_h (nm)	Hydrodynamic diameter (nm)
PAMAM G1	0.086 (0.72)	0.675 (0.28)	0.272	0.77	1.54
PAMAM G3	0.450 (0.51)	3.32 (0.28)	1.85	1.52	3.04

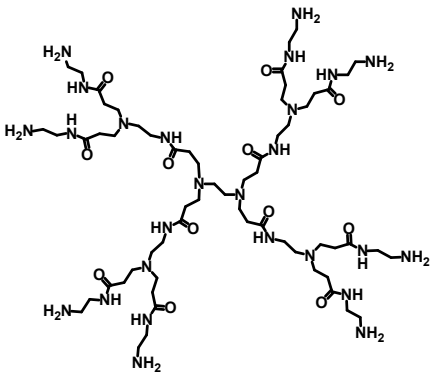
$<\tau>$ = average rotational time; R_h = hydrodynamic radius.

Table S2. Redox parameters and chemical driving force of electron transfer associated with dendrimer-DNT pairs:

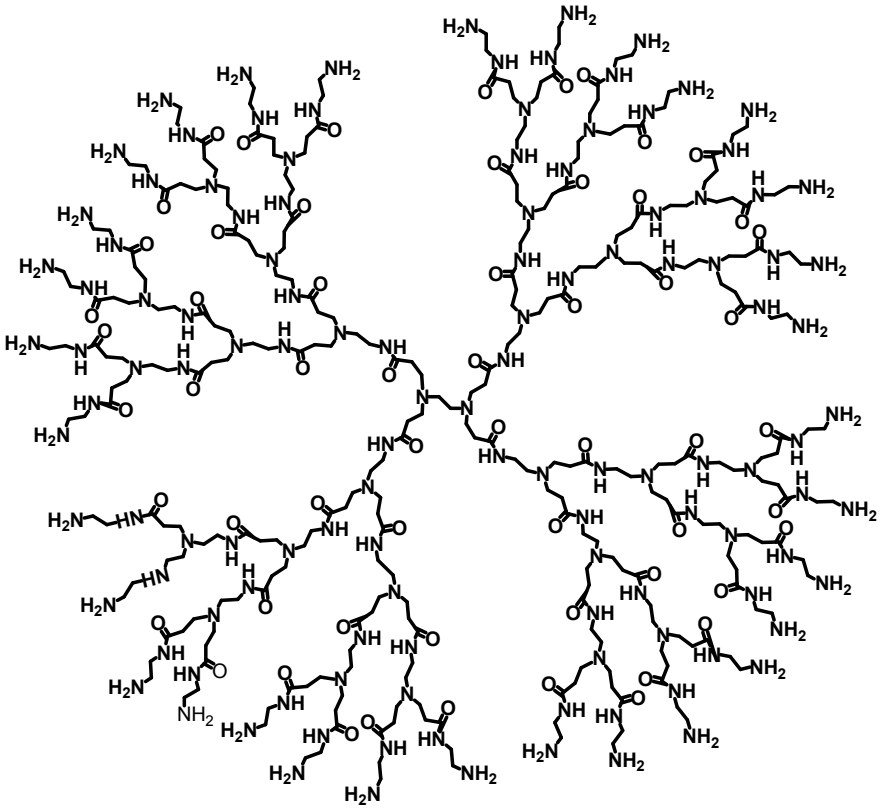
Pairs	E_{ox} (vs SCE)	E_{red} (vs SCE)	E_{00} (eV)	ΔG_{et}(eV)
G1-DNT	1.25V	-1.14V	3.26	-1.03
G3-DNT	1.28V	-1.14V	2.69	-0.41

Scheme

Scheme S1. Chemical structures of both the generation of PAMAM dendrimers used in this study.



PAMAM G1



PAMAM G3

Figures

Figure S1. Fluorescence emission spectra of PAMAM G3 dendrimer when excited at the absorption peak (blue) and when excited at the excitation peak (red)

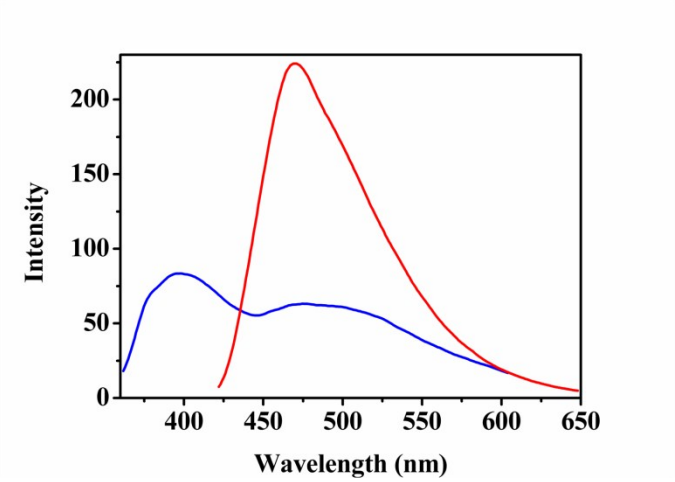


Figure S2. Time resolved anisotropy decay monitoring the intrinsic fluorescence from PAMAM G1 (blue) and PAMAM G3 (red) in methanol.

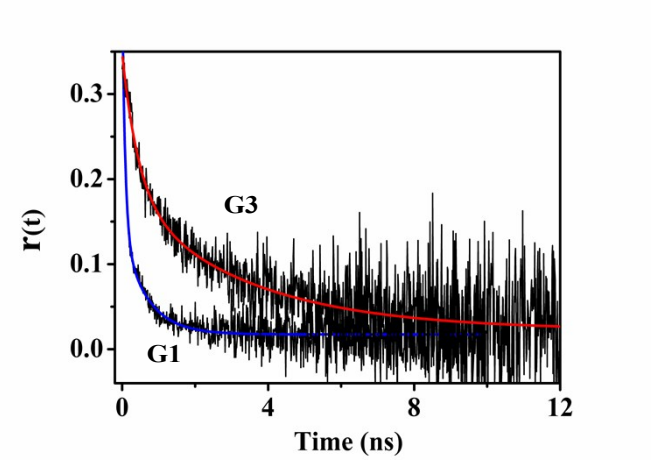


Figure S3. Normalized excitation and emission spectra (exciting at excitation peak) for PAMAM G1 dendrimer in methanol.

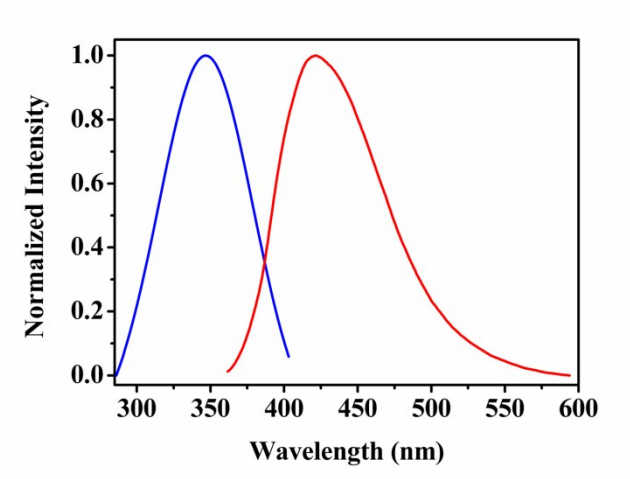


Figure S4. Fluorescence lifetime of the dendrimer after addition of 2,4-DNT in presence of 1(N) HCl solution.