Supporting Information for:

Probing the periphery of dendrimers by heterogeneous electron transfer

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Microelectrode fabrication

A 25 μm diameter Pt wire was inserted into a one side sealed glass capillary. Then the glass was melted to seal the wire. Silver paint was used to make a contact between the Pt and a copper wire. Finally, the glass tip was polished using sand papers to expose the Pt disk. A smooth and clean Pt disk was obtained by polishing the electrode successively in 300 nm and 50 nm alumina powder. The electrode cleanliness was checked by recording a CV using ferrocene as analyte.

Calculation of D_0 and k^0

The D_0 for diarylaminopyrene was determined by following the reported procedure.[1] Microelectrode was used to record chronoamperometry at short times and steady state voltammetry. The slope from the plot of the ratio of current in chronoamperometry and steady state current vs $1/t^{1/2}$ was used to calculate D_0 using the following relation.

$$i_d(t)/ i_{d,ss} = 0.7854+(\pi^{1/2}/4)a(Dt)^{-1/2} \text{ -------- (1)}$$

The D_0 was used in the steady state equation given below to obtain "n"

$$i = 4nFADC \text{ -------- (2)}$$

i = Steady state current
n = Number of electrons transferred
F = Faraday constant
A = Radius of the electrode
D = Diffusion coefficient
C = Concentration of the analyte

The k^0 was calculated from the steady state voltammogram using reported procedure.[2] The $\Delta E_{1/4}$ ($E_{1/4}$-$E_{1/2}$) and $\Delta E_{3/4}$ ($E_{1/2}$-$E_{3/4}$) were obtained from quartile potentials $E_{1/4}$, $E_{1/2}$ and $E_{3/4}$.[2] These values were used to find out a dimensionless parameter λ. By substituting D_0 and λ in equation 3 the k^0 was obtained.

$$k^0 = D_0\lambda/a \text{ --------- (3)}$$

References

1 G. Denuault, M. V. Mirkin and A. J. Bard, *J. Electroanal. Chem.,* 1991, **308**, 27.
2 M. V. Mirkin and A. J. Bard, *Anal. Chem.,* 1992, **64**, 2293.