with amide carbonyl oxygen atoms is likely to lead to strong mixing of the $n\pi^*$ and $\pi\pi^*$ transitions in those amide groups.

In conclusion, some helical structures formed by simple polypeptides in solution may have unusually short main-chain hydrogen bonds. Our calculations indicate that the helicity of such peptides will be over-estimated by CD analysis based on literature calibration of helical content. Whilst much is still to be established, if short hydrogen bonds can form under certain conditions, the use of CD to estimate helicity will have to be complemented by another experimental probe that is sensitive to hydrogen-bond length.

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Orientation Dependence of Energy Transfer in an Anthracene – Porphyrin Donor – Acceptor System**

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The rates of electronic energy transfer (EET) reactions mediated by both dipole–dipole and electron-exchange mechanisms have long been postulated to be critically dependent, amongst other things, on the distance and mutual orientation between the donor and acceptor moieties.[1, 2] Recent experimental validation of these theoretical predictions comes from energy-transfer studies carried out with rationally designed, photochemically active donor–acceptor (D–A) assemblies.[3] Amongst such D–A systems, those based on the porphyrinoid class of chromophores are of relevance to the present work. A number of studies carried out with the covalently/noncovalently linked porphyrin–porphyrin[3b,c, 4] and porphyrin–nonporphyrinic chromophore[5] assemblies have dealt with the effect of D–A distance on the rates of EET reactions but, relatively less attention has been paid to the corresponding orientation effects. In addition, to our knowledge, orientation dependence of EET has not been unequivocally demonstrated in a porphyrin-based system where the donor and the acceptor subunits are disposed at two distinctly different orientations in a given D–A ensemble. Here, we demonstrate the orientation dependence of energy transfer in a simple, porphyrin-based, D–A system **3** where the donor anthracene subunits are linked both at the axial and peripheral sites of a tin(IV) porphyrin scaffold, Scheme 1. Fluorescence-emission and excitation spectra reveal that light absorbed by the "peripheral" anthracene unit of **3** is efficiently transferred to the porphyrin but, that absorbed by the "axial" anthracene subunits is not.

The syntheses of **3** and the corresponding "reference" compounds **1** (where the anthracene subunit occupies only a peripheral position) and **2** (where the anthracene subunits occupy only the axial sites) are illustrated in Scheme 1. These new porphyrins have been characterized by elemental analysis, UV/Vis, ^1H and ^{13}C NMR spectroscopy, and electrochemical methods. In the ^1H NMR spectra, the spacer methylene protons connecting the porphyrin and anthracene chromophores of **1** resonate at $\delta = 6.33$, whereas the corresponding axial methylene protons of **2** resonate at $\delta = 5.65$ a result of the ring-current effect exerted by the basal porphyrin macrocycle. In the spectrum of **3**, resonances arising from the two peripheral and the four axial methylene protons are at $\delta = 6.32$ and 5.62, respectively. The UV/Vis spectra of **1**, **2** and **3** (in CH_2Cl_2) are nearly equivalent to the summation of the

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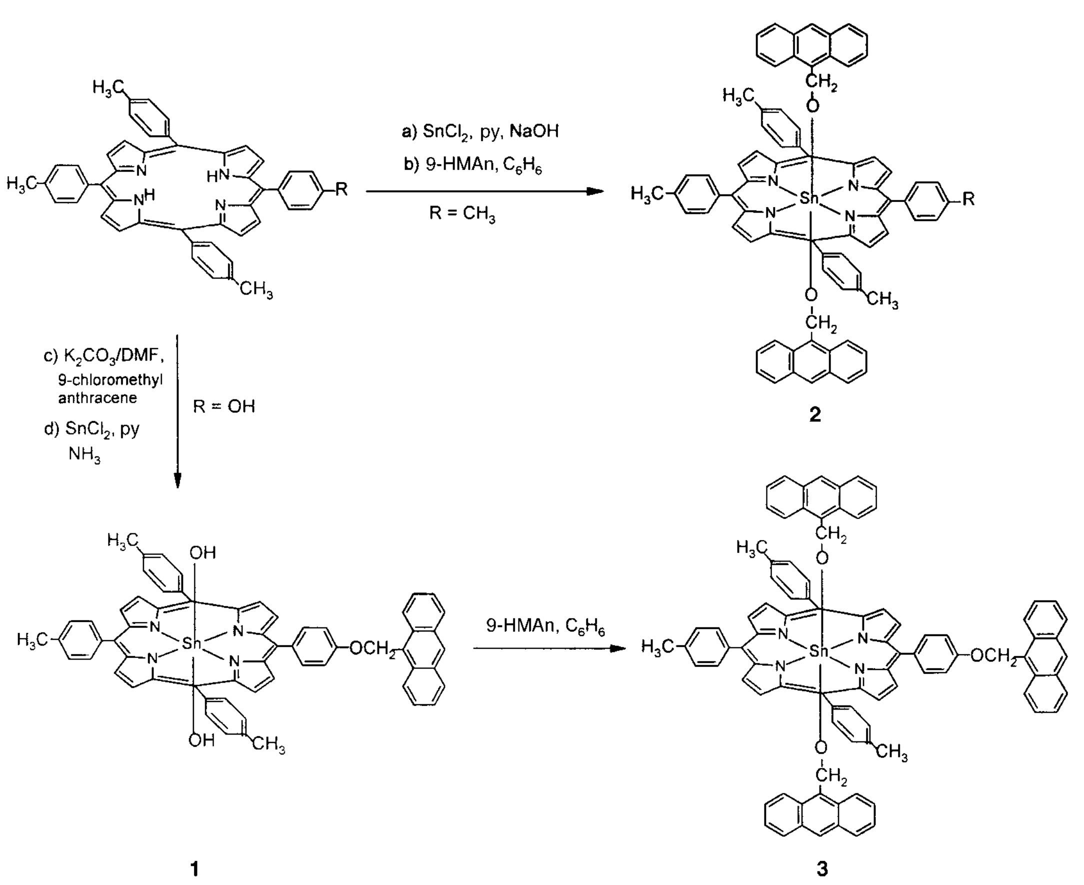

Scheme 1. Synthesis of the three D – A systems investigated; py = pyridine.

spectra recorded for 1:1, 1:2, and 1:3 equivalents (mole/mole) of 5,10,15,20-tetra(*p*-tolyl)porphyrinato tin(IV) dihydroxide ([(ttp)Sn^{IV}(OH)$_2$]) and anthracene (or 9-hydroxymethyl anthracene (9-HMAn)), respectively (Figure 1 a). These spectroscopic data indicate that electronic communication between the porphyrin and the axial/peripheral anthracene π ring systems in these D – A systems is quite insignificant. UV/Vis data additionally suggest that there is scope to individually address the photophysical properties of the porphyrin and anthracene chromophores of **1** – **3** by excitation either in the 500 – 600 nm region or at < 300 nm, respectively.

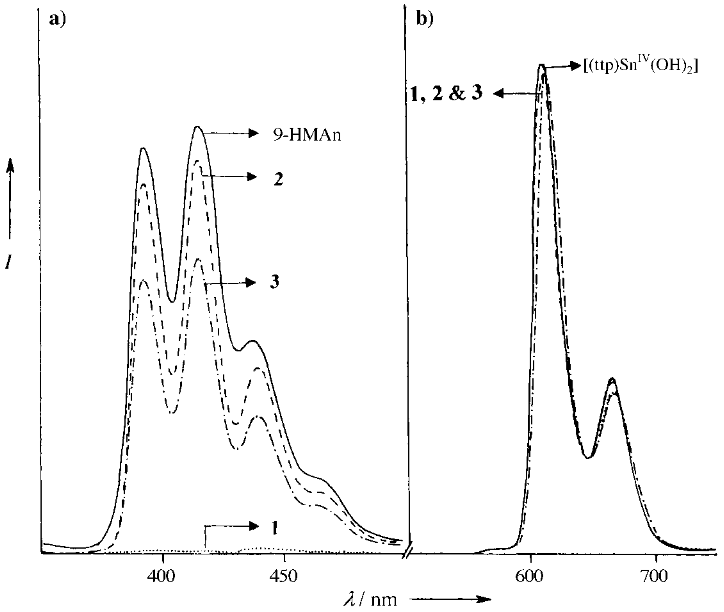

Figure 1. a) Fluorescence spectra of equiabsorbing solutions (O.D. = 0.14) of 9-HMAn, **1**, **2**, and **3** in CH$_2$Cl$_2$ (λ_{ex} = 250 nm); b) fluorescence spectra of equiabsorbing solutions (O.D. = 0.18) of [(ttp)Sn^{IV}(OH)$_2$], **1**, **2**, and **3** in CH$_2$Cl$_2$ (λ_{ex} = 525 nm); O.D. = optical density.

Irradiation into the porphyrin absorption band (525 nm) of CH$_2$Cl$_2$ solutions of these molecular systems resulted in fluorescence quantum yields that are close ($\Phi = 0.047 - 0.048$) to the quantum yield of [(ttp)Sn^{IV}(OH)$_2$] ($\Phi = 0.048 \pm 0.004$), Figure 1 b. On the other hand, excitation at the anthracene absorption maximum (250 nm) resulted in quenching of fluorescence for **3** ($\Phi = 0.21 \pm 0.01$) and also **1** ($\Phi < 0.001$) compared to the fluorescence of 9-HMAn ($\Phi = 0.32 \pm 0.02$). Interestingly, fluorescence arising from the anthracene subunits of **2** was largely unaffected ($\Phi = 0.29 \pm 0.02$) under similar experimental conditions, Figure 1 a.[6] The quenching efficiencies ($\%Q = \{[\Phi_{9\text{-HMAn}} - \Phi_{1,2,\text{or}3}]/\Phi_{9\text{-HMAn}}\}100$) for the anthracene units of **1** – **3** are estimated (±7 %) to be ~99, 9, and 34, respectively.

Fluorescence life times (±10 %) of the anthracene chromophores (λ_{ex} = 250 nm, λ_{em} = 400 nm) of these D – A systems are: **1**, 0.16 ns (~100 %); **2**, 2.14 ns (100 %), and **3**, 0.62 ns (31 %) and 2.28 ns (69 %), the values in the parentheses are the relative amplitudes obtained while fitting the data to one/two exponential decay functions. The one-exponential decays observed for tin(IV) porphyrin based D – A systems **1** and **2** are unlike those of the several free-base porphyrin–anthracene systems reported by us earlier.[7] The biexponential fluorescence decay observed for the latter systems, in which the porphyrin and anthracene are connected by a flexible -OCH$_2$-linkage (at the "peripheral sites"), has been interpreted in terms of the presence of two different D–A conformers ("closed" and "extended") that do not equilibrate within the life time of the fluorophore. Clearly, the single exponential decay of the analogous tin(IV) porphyrin based systems **1** and **2** indicates that such a conformational equilibrium does not play a significant role in these cases.[8] Based on the data of **1** and **2**, the biexponential decay of **3** can be rationalized in terms of the presence of two different ground-state D–A orientations (unquenched axial and quenched peripheral) in this system.

Excitation of both **3** and **1** at 250 nm resulted in the appearance of well-defined porphyrin emission bands in the 600–700 nm region; this was not the case for **2**. In addition, overlap of the corrected and normalized excitation spectra (emission collected at the porphyrin emission maximum, 665 nm) with the corresponding absorption spectra reveals that fluorescence quenching is entirely a result of the energy transfer in these two D–A systems (Figure 2). The energy-transfer efficiencies (%E) for **1** (99 ± 7) and **3** (25 ± 3) are quite close to the corresponding %Q values (see above). There was no indication of any energy transfer in **2** (see Figure 2, %E = 5 ± 2) consistent with the high fluorescence observed for this system.

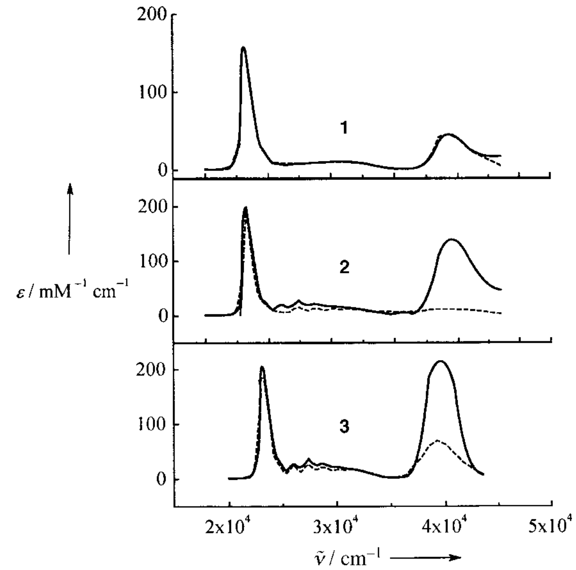

Figure 2. Overlay of the excitation (----) and absorption (——) spectra of **1**–**3** in CH$_2$Cl$_2$ (λ_{em} = 665 nm). The excitation spectra were corrected for the instrument response function and were normalized with respect to the absorption spectra between 22222–25000 cm^{-1}.

Thus, energy transfer is lacking in **2** (where the donor subunits are *exclusively* at the axial positions), almost quantitative in **1** (where the donor subunit is *exclusively* at the peripheral site), and is approximately 30% in **3** (where two donor subunits are at the axial site and one at the peripheral position). Clearly, energy transfer to the porphyrin is strongly favored (~100%) from the peripheral anthracene and is quite inefficient (~0%) from the axial anthracene in these D–A systems. It should be noted here that the peripheral anthracene subunit of **3** absorbs only one third of the incident light at the excitation wavelength. Thus, a near 30% quenching observed for this system amounts, actually, to %E ~100 from the peripheral anthracene to the porphyrin.[9]

Having demonstrated the orientation dependence of EET in these D–A systems, it is pertinent to explore the origin of this novel effect. The Dexter's exchange mechanism requires the presence of electronic communication between the donor and acceptor species (via orbital overlap).[2] However, the ^{1}H NMR and UV/Vis data discussed above indicate that such interaction in these intramolecular porphyrin–anthracene compounds is quite insignificant. Therefore, we chose to analyze the EET in **3** by the dipole–dipole mechanism, according to which the rate of EET, k_{Forster}, is given by Equation (1).[1]

$$k_{\mathrm{Forster}} = [8.8 \times 10^{-25} \kappa^2 \Phi_{\mathrm{D}} J_{\mathrm{Forster}}]/[n^4 \tau R^6] \quad (1)$$

In Equation (1) n is the solvent refractive index, Φ_{D} and τ are the fluorescence quantum yield and the fluorescence lifetime of the isolated donor (anthracene), J_{Foster} is the Forster's overlap integral representing emission of anthracene and absorption of the acceptor ([(ttp)Sn$^{\mathrm{IV}}$(OH)$_2$]) components, R is the D–A center-to-center distance, and κ^2 is the so-called orientation factor. While J_{Foster} (=1.2 × 10^{-13} cm^6 m mol^{-1}), Φ_{D} (=0.24) and τ (5.2 ns) are the same for both axially and peripherally substituted situations, the center-to-center distances between the tin(IV) ion and the axial and equatorial anthracene rings in **3** are estimated to be 6.5 and 9.5 Å, respectively.[10] We thus note that, assuming the same κ^2 (=2/3, for a random D–A orientation), the Forster energy transfer to the porphyrin should, in principle, be more conducive from the axial anthracenes than it is from the peripheral anthracene according to Equation (1).[11] This is clearly not the case as revealed by the %E values given above. Thus, κ^2 [Eq. (2)] plays a key role in determining the directionality of EET in **3**.

$$\kappa^2 = [\cos\gamma - 3\cos\alpha\cos\beta]^2 \quad (2)$$

In Equation (2) α and β are the angles made by the transition dipoles of anthracene (axial/peripheral) and porphyrin with the line joining the centers of the transitions and γ is the angle between the two transition dipoles. While the transition dipole of the emitting ^{1}S state of anthracene lies on the short axis of the molecule,[12] that of porphyrin is known to lie along a line joining two opposing pyrrole nitrogens.[13] Thus, the near perpendicular juxtaposition of the donor and acceptor transition dipoles when the anthracenes occupy the axial sites and the near coplanar situation when the anthracene is linked at the peripheral site seem to be modulating the κ^2 in such a way that the energy transfer is nearly absent in **2** and is almost quantitative in **1**.[14] The unique behavior of compound **3**, wherein the anthracene donors are connected both at the axial and peripheral sites is thus self explanatory.

In summary, to our knowledge, D–A compound **3** is the first porphyrin-based system wherein the donor species are connected both at the axial and peripheral positions of the macrocycle. Energy transfer occurs only from the peripheral anthracene to the porphyrin in this system. We believe that realization of such an orientation dependence of EET would amount to demonstration of unidirectionality of the energy transfer event.[15]

Experimental Section

Materials were obtained from either Aldrich Chemicals (USA) or BDH (India). Measurements of absorption, steady-state fluorescence and excitation, and ^{1}H and ^{13}C NMR spectra (200 or 400 MHz) and also the time-resolved fluorescence decays were carried out as detailed previously.[7, 16] Fluorescence quantum yields (Φ) were estimated using either 5,10,15,20-tetraphenylporphyrinato zinc(II) (for $\lambda_{ex} = 525$ nm, porphyrin band) or anthracene ($\lambda_{ex} = 250$ nm, anthracene band) as standards.

Syntheses: **1** (0.05 g, 0.05 mmol; obtained, in 82% yield, by tin insertion into 5-(4-(9-methyloxy anthracenyl)phenyl)-10,15,20-tri(*p*-tolylporphyrin)) and 9-HMAn (0.05 g, 0.24 mmol) were dissolved in dry C_6H_6 (20 mL). The resulting mixture was refluxed under a nitrogen atmosphere for 12 h. Solvent was evaporated under reduced pressure and the residue was redissolved in minimum amount of $CHCl_3$ and purified by flash column chromatography on an alumina column. The purple (second) fraction was collected by eluting with $CHCl_3$. Evaporation of the solvent and recrystallization from $CHCl_3$/hexane afforded **3** in 73% yield.

Compound **2** was synthesized by refluxing $[(ttp)Sn^{IV}(OH)_2]$ and 9-HMAn in benzene and purified in a manner analogous to that described above for **3**. Yield: 74%.

Characterization (selected data) **3**: ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): $\delta = 9.25$ (m, 8H, β-pyrrole), 8.58 (m, 4H, anthracene), 8.38 (m, 8H, anthracene), 8.18 (m, 9H, tolyl and anthracene), 8.05 (m, 6H, tolyl and anthracene), 7.55 (m, 16H, tolyl and anthracene), 6.32 (s, 2H, $-OCH_2$, *peripheral*), 5.65 (s, 4H, $-OCH_2$, *axial*), 2.75 (s, 9H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS): 63.4 ($-OCH_2$, *peripheral*), 57.2 ($-OCH_2$, *axial*); UV/Vis (CH_2Cl_2): λ_{max} [nm] ($\log\varepsilon$): 607 (4.15), 565 (4.12), 525 (3.50), 429 (5.36), 255 (5.36); elemental analysis (%) calcd for: $C_{92}H_{66}N_4O_3Sn$: C 79.25, H 4.77, N 4.02; found: C 79.11, H 4.62, N 4.55; cyclovoltammetry: $E_{1/2}$ (CH_2Cl_2, 0.1M TBAP (tertabutyl ammonium perchlorate); [V] versus SCE (saturated calomel electrode)): 1.60, 1.38, −0.92, −1.32.

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[9] This analysis implicitly assumes that singlet energy migration between the axial and equatorial anthracenes in **3** is negligible.

[10] Molecular structures of these compounds have been modeled using the PM3 calculations. The PM3 minimized structures reveal that, at the axial sites of **3** (and also **2**), the dihedral angle $Sn\text{-}O\text{-}C\text{-}C_{anthracene}$ and the angle Sn-O-C are 165.5° and 120.8°, respectively. The corresponding dihedral angle $C_{meso}\text{-}O\text{-}C\text{-}C_{anthracene}$ and the angle $C_{meso}\text{-}O\text{-}C$, at the peripheral sites of **3** (and also **1**), are 104.4° and 125.6°, respectively. Thus, there is a near perpendicular juxtaposition of the porphyrin and the axial anthracene subunits in **3**, probably because the corresponding "nonperpendicular" orientations are sterically unfavorable in this crowded system. By contrast, changing the dihedral angle between the porphyrin and equatorial anthracene can potentially generate many energetically close rotamers that are not sterically unfavorable.[7]

[11] Indeed, assuming that $\kappa^2 = 2/3$, the energy-transfer rate from the axial anthracene to the porphyrin has been estimated to be an order of magnitude faster than it is from the peripheral anthracene (calculations were performed using PhotochemCAD: H. Du, R.-C. A. Fuh, J. Li, L. A. Corkan, J. S. Lindsey, *Photochem. Photobiol.* **1998**, *68*, 141).

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[14] The value of κ^2 estimated for the PM3 minimized structure is as low as 0.0004 for the porphyrin–axial-anthracene pair and is quite high (1.28) for the porphyrin–peripheral-anthracene pair. However, given the "semi-rigid" nature of the link between the two chromophores in **3**, our estimation of the magnitudes of the κ^2 values may not be rigorous. Nonetheless, the above analysis suggests that the directionality conditions of the dipole–dipole mechanism clearly do not favor Forster energy transfer between the axial anthracenes and the basal porphyrin. Notwithstanding this, other explanations (e.g. those involving the tin(IV) center) that do not invoke the κ^2 dependence of energy transfer and yet rationalize the absence of energy transfer in the axial direction in **2** and **3** cannot be ruled out altogether.

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