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Novel covalently linked porphyrin dimers for controlled intramolecular energy transfer

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Abstract

Dimers constituting differing porphyrin basicities undergo selective demetallation or protonation of one unit of the dimer. The efficiency of singlet excited energy transfer from neutral free-base/zinc(II) porphyrin to diprotonated porphyrin unit could be fine tuned by varying acidity in the covalently linked dimers. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Covalently linked porphyrin dimers have furnished important models to elucidate mechanisms of excitation energy transfer and photoinduced electron transfer in natural photosynthetic processes [1–8]. In addition, some of these models are potentially important materials for use in molecular-scale electronic devices [9–11]. Recently, a molecular optoelectronic gate consisting of an array of porphyrins has been reported [12]. Two basic photophysical properties have been exploited in the design of molecular devices, (i) singlet–singlet energy transfer and (ii) photoinduced electron transfer. We made use of the differential basicity of the inner imino nitrogens of the meso-fluoroarylporphyrin and meso-tetraphenylporphyrin to construct simple dimeric porphyrins wherein absorption of a photon of visible light by a neutral porphyrin leads to an emission of a photon from diprotonated porphyrin with very high efficiency ($\geqslant 95\%$). The occurrence of such processes can be easily tuned by the acidity of the medium, fundamentals of which could be used the in construction of artificial photonic devices.

The substitution of pentafluoroaryl groups in the meso positions of the porphyrin confers unique inertness of the inner imino nitrogens towards protonation and metallation reactions. The fluoroarylporphyrins exhibit interesting optical and electrochemical properties [13]. We synthesised porphyrin dimers (Fig. 1) comprising of meso-fluoroarylporphyrin and meso-tetraphenylporphyrin with an ethylenedioxide covalent bridge to accomplish selective protonation and demetallation of the meso-tetraphenylporphyrin moiety in the dimer. We demonstrate here that the dicationic porphyrin dimer exhibits efficient intramolecular singlet excitation energy transfer (eet) from

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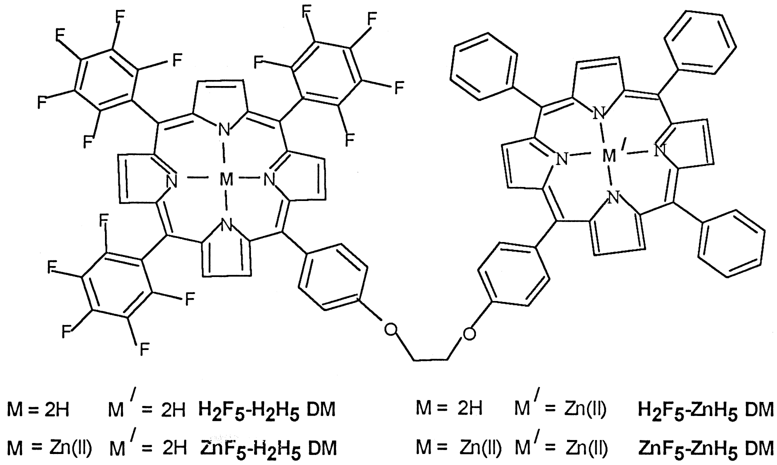

Fig. 1. Structure of the dimer porphyrins.

unprotonated fluoroarylporphyrin to diprotonated tetraphenylporphyrin moiety.

2. Experimental

Covalently linked porphyrin dimer was synthesised by the method of Little [14]. We have used 5-(4-methoxyphenyl)-10,15,20-triphenylporphyrin ($H_2H_5OCH_3$) and 5-(4-methoxyphenyl)-10,15,20-tri(pentafluoro)phenylporphyrin ($H_2F_5OCH_3$) as reference compounds for comparison studies. Hereafter these two porphyrins will be designated as tetraphenylporphyrin and fluoroarylporphyrin, respectively. 5-(4-Hydroxyphenyl)-10,15,20-tri(pentafluoro)phenylporphyrin (H_2F_5OH) was prepared by demethylation of the corresponding methoxyporphyrin obtained from pyrrole and a mixture of respective benzaldehydes [15]. All the free-base porphyrins were characterised by UV–VIS., ^{1}H-NMR and FAB-MS spectroscopies. For absorption, fluorescence and metallation studies, a mixture of dichloroethane and methanol (dce/MeOH; 1:1; v/v) was used as a solvent. Electrochemical and ^{1}H-NMR measurements were performed in CH_2Cl_2 and $CDCl_3$ as solvent, respectively.

It is found that one of the porphyrin units of H_2F_5–H_2H_5 DM can be selectively metallated with zinc(II) acetate at room temperature to yield H_2F_5–ZnH_5 DM. However, the di-zinc(II) derivative (ZnF_5–ZnH_5 DM) was obtained by refluxing H_2F_5–H_2H_5 DM with excess zinc(II) salt. Interestingly, the treatment of ZnF_5–ZnH_5 DM with ca. 1 M trifluoroacetic acid (TFA) in a mixture of solvents results in demetallation of the tetraphenylporphyrin unit of the dimer. The spectral characteristics of the partially metallated bis-porphyrins were compared with the bis-porphyrins prepared from appropriate free-base and metallated porphyrin monomers.

The kinetics of zinc(II) ion incorporation into the free-base porphyrins [16–18] in a binary solvent mixture of dichloroethane and methanol (1:1, v/v) containing 0.1 M $NaClO_4$ solution at 300 K was studied using optical absorption spectral method. The decrease in the absorbance of the Q band around 500 nm of the free-base porphyrin was monitored as a function of time. It was found that at this wavelength neither the metallated porphyrins nor the metal salt absorb. The concentration of the porphyrins was held constant ($\sim 10^{-5}$ M) and the concentration of zinc(II) acetate was varied from (10–40 mM) maintaining pseudo-first-order conditions. A minimum of five different metal ion concentrations were investigated for each porphyrin. Plots of $1n((A_0 - A_\alpha)/(A_t - A_\alpha))$ versus time (t), where A_0, A_t and A_α represent the absorbance at time ($t = 0$), time (t) and at the time of completion of the reaction respectively. Good linearity was observed for all the metal ion concentrations. The pseudo-first-order rate constant (k_{obs}) values were calculated from the slope of

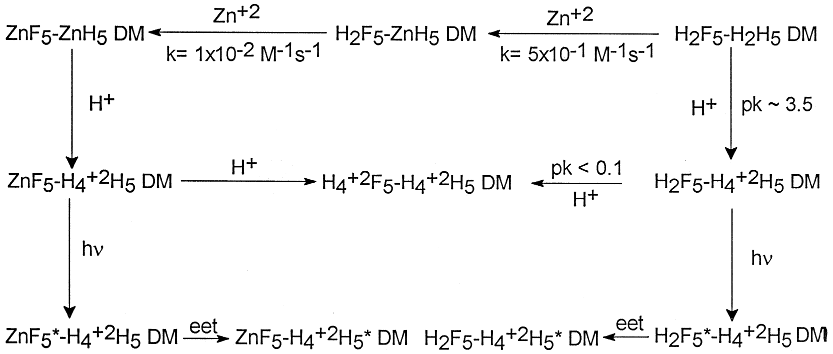

Fig. 2. Schematic representation of different processes of dimer porphyrins.

these plots. The overall second-order rate constant (k) was determined from the linear plot of $\log(k_{obs})$ versus $\log([M(II)])$. The k values are found to be 1×10^{-2} and 5×10^{-1} M^{-1} s^{-1} for the insertion of Zn(II) ions into the $H_2F_5OCH_3$ and $H_2H_5OCH_3$ porphyrins respectively. The sequence of metallation and demetallation processes are shown in Fig. 2.

3. Results

3.1. Absorption spectroscopy

The optical absorption spectra of the bis-porphyrins are compared with those of the monomeric constituents and intermolecular mixtures of these species. The absorption spectral data of the porphyrins in presence and absence of TFA are given in Table 1. It is observed that the UV–VIS spectra of the covalently linked dimer is superimposable with the absorption spectra of its constituent monomers indicating that the porphyrin units of the dimer behave independently. The protonation equilibria of the monomeric and dimeric species were studied in a mixture of solvents (1:1, v/v, dce/MeOH). Gradual addition of acid (TFA) to a solution of $H_2H_5OCH_3$, results in the changes of absorption spectrum until a acid concentration of 0.07 M is reached leading to the formation of diprotonated meso-tetraphenylporphyrin ($H_4^{+2}H_5OCH_3$). The $H_2F_5OCH_3$ under the same conditions remain indefinitely stable in acidic solution (0.1 M) without protonation. At higher concentration of acid ($\gg 0.1$ M), however, the fluoroarylporphyrin species gets protonated as revealed from its characteristic absorption bands (442, 586 and 652 nm). These observations indicate that the dimer in solution in presence of 0.1 M TFA, would be selectively and quantitatively protonated resulting in the formation of diprotonated tetraphenylporphyrin moiety. Interestingly, the absorption spectrum of the partially protonated dimer covers significantly the entire visible region of electromagnetic radiation unlike the spectra of the neutral or completely protonated dimer porphyrins. It is found that the zinc(II) derivative of tetraphenylporphyrin, ZnH_5OCH_3 is readily demetallated forming a diprotonated species in presence of 1 M TFA whereas the corresponding fluoroarylporphyrin, ZnF_5OCH_3, remains intact without any demetallation and protonation under the same conditions. It is of interest to note that successive addition of acid to the di-zinc(II) dimer (ZnF_5–ZnH_5 DM) followed by neutralisation leads to the formation of partially demetallated derivative (ZnF_5–H_2H_5 DM) as revealed from its absorption spectrum. The formation of this species was confirmed by comparing the spectrum with that of the dimer obtained from the condensation of the corresponding free-base tetraphenylporphyrin with zinc(II) derivative of fluoroarylporphyrin.

3.2. Fluorescence spectroscopy

The free-base porphyrin dimer and the monomeric porphyrin units exhibit two emission bands in the region ~ 650 and 720 nm corresponding to Q(0,0) and Q(0,1) transitions, respectively. The diprotonated porphyrin units are characterised by a single emission band around 690 nm [19]. It is seen that the

Table 1
Optical and electrochemical redox data of the monomer and dimer porphyrins at 300 K

Compound	λ_{abs} (nm; log ε)[a]	λ_{em} (nm)[b]	E_{redox} (mV)[c]	J ($\times 10^{11}$ mol^{-1} cm^{6})	k_{eet} ($\times 10^{9}$ s^{-1})
$H_2F_5OCH_3$	415(5.45), 509(4.28), 543(3.60), 584(3.82), 640(3.23)	644, 707	900, 1085, -1325, -1730		
$H_2F_5OCH_3^{d}$	415(5.45), 509(4.28), 542(3.62), 584(3.82), 640(3.23)	644, 707			
$H_2H_5OCH_3$	417(5.45), 515(4.04), 550(3.75), 591(3.55), 646(3.49)	650, 714	500,800, -1675, -2000		
$H_2H_5OCH_3^{d}$	442(5.30), 564(3.40), 609(3.80), 662(4.48)	700			
H_2F_5–H_2H_5 DM	417(5.47), 510(4.23), 547(3.64), 588(3.74), 644(3.35)	650, 708	500, 915^{e}, 1120, -1340, -1720^{e}, -2000		
H_2F_5–H_2H_5 DM^{d}	416(5.29), 442(4.97), 509(4.12), 542(3.56), 585(3.78), 661(4.14)	644(sh), 698		41.2	89.5
ZnF_5–H_2H_5 DM	421(5.82), 514(4.16), 552(4.42), 589(3.81), 645(3.50)	600, 651,712	490, 650, 710, 920, -1550, -1660, -1935^{e}	2.05	6.44
ZnF_5–ZnH_5 DM	424(5.81), 555(4.43), 596(3.88)	605, 652	330, 690^{e}, 950, -1600, -1920^{e}, -2195		
ZnF_5–ZnH_5 DM^{d}	421(5.69), 441(5.41), 553(4.30), 660(4.52)	696		26.9	82.0

[a] In 1:1 (dce/MeOH, v/v).

[b] In 1:1 (dce/MeOH, v/v), λ_{ex} values were 505 and 540 nm for the free-base porphyrins and their zinc(II) derivatives, respectively.

[c] Electrochemical redox data of the porphyrins in CH_2Cl_2 solution containing 0.1 M $TBAPF_6$. Potential values are referenced to internal Fc^{+}/Fc couple. All the potentials observed involves one electron oxidation/reduction processes unless otherwise mentioned.

[d] In presence of TFA acid.

[e] Involves more than one electron process.

fluorescence profile of the free-base porphyrin dimer is exactly reproduced in the emission profile of an intermolecular mixture of the constituent monomeric units. It is remarkable that in presence of acid (TFA, 0.1 M), the fluorescence emission of the free-base porphyrin dimer (H_2F_5–H_2H_5 DM) exhibit only one emission band around 690 nm corresponding to the presence of protonated tetraphenylporphyrin unit, although the excitation wavelength is 505 nm where the extinction coefficient value of unprotonated fluoroarylporphyrin is maximum. This observation contrasts significantly from the emission profile of the protonated solution containing intermolecular mixture of the monomeric units wherein two emissions are observed. This fluorescence behaviour of the protonated dimer indicates that all the excitation energy is transferred to the protonated porphyrin unit. The zinc(II) derivatives of the monomeric porphyrin units and of the dimer are characterised by their two emission bands at ~ 600 and 650 nm. It is found that in presence of 1 M TFA, the emission profile of ZnF_5OCH_3 remains unchanged indicating absence of demetallation and protonation reactions. On the other hand, the emission spectrum of ZnH_5OCH_3 in 1 M TFA, exhibits a single emission band around 690 nm corresponding to the protonation of the tetraphenylporphyrin unit. It is of interest to note that the di-zinc(II) dimer, ZnF_5–ZnH_5 DM in presence of 1 M TFA revealed a single emission band around 690 nm while an equimolar mixture of ZnF_5OCH_3 and ZnH_5OCH_3 in TFA (1 M) exhibit emissions arising from ZnF_5OCH_3 and $H_4^{+2}H_5OCH_3$ units (Fig. 3). This suggests that a covalent linkage between the porphyrin units provides an additional

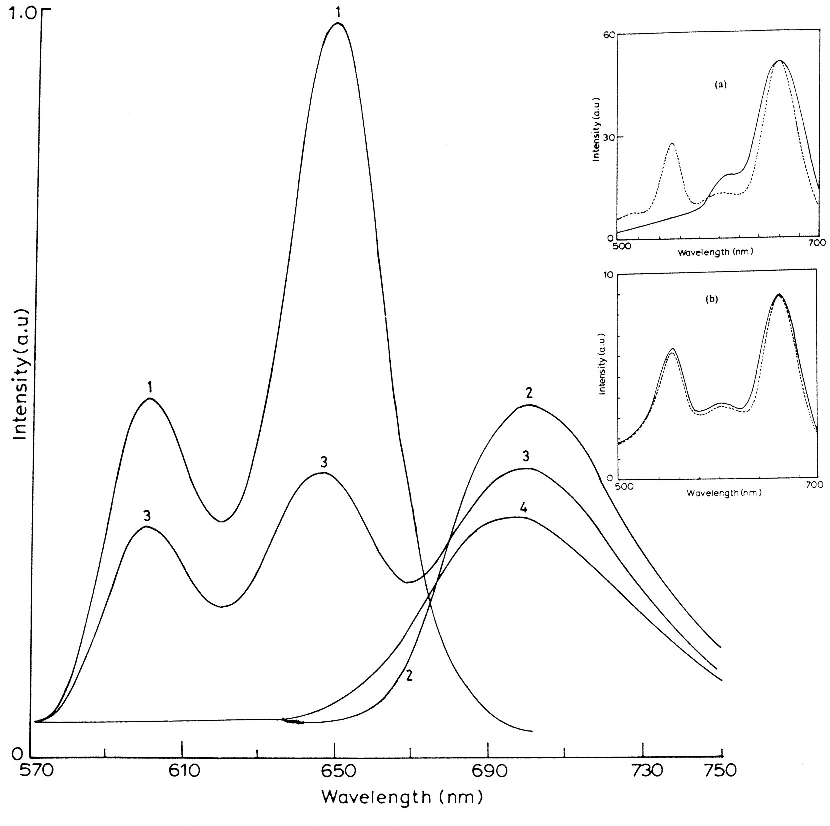

Fig. 3. The fluorescence emission spectra (λ_{ex} at 540 nm) of zinc(II) derivatives of the porphyrins in presence of 1 M TFA (1:1, CH_2Cl_2: MeOH, v/v): (1) ZnF_5OCH_3, (2) ZnH_5OCH_3, (3) intermolecular mixture of ZnF_5OCH_3 and ZnH_5OCH_3 and (4) ZnF_5–ZnH_5 DM. Inset shows the comparison of the corrected excitation spectrum (solid line) and absorption spectrum (dotted line) of the (a) intermolecular mixture of ZnF_5OCH_3 and ZnH_5OCH_3 and (b) ZnF_5–ZnH_5 DM.

decay pathway for the excited singlet state of the unprotonated porphyrin unit. By excitation spectroscopy the dependence of the intensity of the porphyrin emission on the excitation wavelength is detected. The emission was monitored at a wavelength 700 nm where the majority of the fluorescence arises from the diprotonated tetraphenylporphyrin. The excitation spectra of the free-base porphyrin dimer, its zinc(II) derivatives, intermolecular mixture of the monomeric porphyrin units and their zinc(II) derivatives are recorded and representative spectra are shown in the inset of Fig. 3. It is clear that the absorption of light by unprotonated fluoroarylporphyrin unit in the dimer contributes significantly to the emission of the protonated unit. Interestingly, the ratio of relative fluorescence peak intensities of equimolar mixture of free-base monomer porphyrins and its zinc(II) derivatives in acidic solution is found to be dependent on the excitation wavelength. This is in contrast to that found for the emission of partially protonated free-base porphyrin dimer and its zinc(II) derivatives. These observations is indicative of an excitation energy transfer from the excited singlet state of neutral fluoroarylporphyrin to the diprotonated tetraphenylporphyrin unit.

4. Discussion

The covalently linked dimers exhibit marginal shift in absorption bands accompanied by reduced ε values relative to the admixture of monomeric constituents. This indicates a weak electronic interaction between porphyrin rings of the dimer caused by the steric distortion of the covalent linkage. Electrochemical redox data of the dimers are characteristic with the appearance of one electron ring oxidation and reductions of the constituent monomer porphyrin units. The magnitude of redox potentials of dimers are marginally shifted relative to that observed for the individual porphyrins indicating weak interaction between the two porphyrin rings (Table 1). The charge transfer energies (E_{CT}) of the dimers, $H_2F_5^{-\cdot}$–$H_2H_5^{+\cdot}$ DM, $ZnF_5^{-\cdot}$–$H_2H_5^{+\cdot}$ DM, $ZnF_5^{-\cdot}$–$ZnH_5^{+\cdot}$ DM calculated from electrochemical redox data lie in the range of 1850–2000 MeV as compared to the energies of the first singlet excited state of porphyrins in the range of 1900–2100 MeV. This suggests weak exergonicity for photoinduced electron transfer reactions in these dimers which compete with the excitation energy transfer. Brookfield et al. [20] has reported an excitation energy transfer from Zn-porphyrin to the free-base porphyrin for a series of covalently linked Zn–H_2 porphyrin dimers with different chain length ($n = 2 \ldots 6$). In these systems an appreciable amount of excitation light (30% at λ_{ex} 550 nm) is directly absorbed by the free-base porphyrin (H_2P) unit in the dimer and hence not available for energy transfer. In the present study, the excitation wavelengths used are at 505 and 540 nm depending on the nature of the protonated dimer, H_2F_5–$H_4^{+2}H_5$ DM or ZnF_5–$H_4^{+2}H_5$ DM. At these λ_{ex} values, the protonated porphyrin has least absorption and hence all the excitation energy is efficiently transferred to the emission of protonated porphyrin unit of the dimer. Photoexcitation of an intermolecular mixture of monomers in acid solution at the distinct absorption maxima of the unprotonated species results in the emission spectrum of the excited species. The emission spectrum observed for the porphyrin dimers is found to be independent of excitation wavelength. The highly efficient singlet–singlet energy transfer in the partially protonated dimer is confirmed by the corrected excitation spectra of the dimers. The excitation spectrum (after normalisation at λ_{max} of 660 nm of diprotonated porphyrin) coincides with the absorption spectrum of the partially protonated dimers. This demonstrates that the energy transfer is almost quantitative. The photophysical investigations reveal efficient energy transfer in the partially protonated dimers and this essentially proceeds through intramolecular mechanism. The Forster mechanism describes the energy transfer between the donor and acceptor substituents through space and hence direct contact between the donor and acceptor is not required. This mechanism is applicable to the dimers reported here considering that the individual donor/acceptor porphyrin units retains their spectroscopic identity owing to weak electronic coupling between the molecular subunits. The average donor–acceptor distance (R_0) at which the rate constant for energy transfer (k_{eet}) equals the rate constant for non-radiative decay of the donor is determined using Forster equation [21].

$$R_0^6 = \frac{9(\ln 10)\,\kappa^2 \Phi_D J}{128\pi^5 N \eta^4} \tag{1}$$

where Φ_D = fluorescence quantum yield of the donor in the absence of acceptor, η is the refractive index of the solvent (taken as 1.36, calculated from the η values of dichloroethane and methanol), N is Avogadro's number and κ^2 is the orientation factor which is equal to 2/3 for random geometries. The numerical value of overlap integral, J is calculated from the equation,

$$J = F_D(\nu)\,\varepsilon(\nu)\,\nu^{-4}\,d\nu \tag{2}$$

where $F_D(\nu)$ is the fluorescence intensity of the donor in wavenumber units with total intensity normalised to unity, $\varepsilon(\nu)$ is the absorption coefficient of the acceptor and ν is the wavenumber in cm^{-1}. The overlap integral values (J) for the dimers in presence of acid is found to be one order of magnitude higher than those found for neutral dimers. Representative J values are given in Table 1. Substituting the J values in Eq. (1) yields R_0 values of 48.1 and 35.6 Å for the dimer H_2F_5–$H_4^{+2}H_5$ DM and ZnF_5–$H_4^{+2}H_5$ DM, respectively, and 23.2 Å for the unprotonated dimer ZnF_5–H_2H_5 DM. These data show that singlet energy transfer can occur over quite large distances. The rate of energy transfer k_{eet} is related to the experimentally determined radiative lifetime of the donor (τ_D) and the ratio of the critical Forster distance (R_0) to the distal separation between the chromophores in the dimer (R_{DA}) as,

$$k_{eet} = 1/\tau_D(R_0/R_{DA})\,. \tag{3}$$

The donor and acceptor porphyrins in the dimers are assumed to have various distances due to flexible covalent linkage. Space filling modelling studies of the dimer have revealed that the centre-to-centre distance of the 'closed conformer' is estimated to be 13 Å and that of the completely 'extended conformer' is about 20 Å. It is reasonable to assume that in solution the equilibrium geometry of the conformers could have a centre to centre distance of ca. 16 Å. The rate constant calculated using these values are given in Table 1. It is noteworthy that the magnitude of k_{eet} values are found to be much larger for the partially protonated dimers relative to that observed for the neutral dimers. This clearly indicates that a critical pH control of the dimers bring forth enhanced excitation energy transfer. The large magnitude of R_0 ($>$ 20 Å) and high rates of energy transfer are consistent with Forster's inductive resonance mechanism of energy transfer in these systems. It may be pointed out that the energy transfer occurring through Dexter mechanism requires direct contact between donor and acceptor electronic orbitals. In the dimers reported here Dexter transfer is unlikely since the orbitals of the covalent linking group (essentially σ type) do not permit super exchange or through bond interaction [22].

5. Conclusion

The synthesis and characterisation of simple hetero nuclear free-base/di-zinc(II) porphyrin dimers have been accomplished. The two units of the dimer molecule exhibit different basicity values as evidenced from the relative rates of metal incorporation reactions. The difference in metallation/protonation behaviour of the two moieties bring forth the spectral distinction between the two covalently linked chromophores. Quantitative protonation of one part of the dimer in presence of strong acid lead to the formation of partially protonated dimer which displays an efficient intramolecular excitation energy transfer upon photoexcitation. The partially protonated species, H_2F_5–$H_4^{2+}H_5$ DM and ZnF_5–$H_4^{2+}H_5$ DM can be converted to fully protonated species $H_4^{2+}F_5$–$H_4^{2+}H_5$ DM by increasing the acid strength beyond 1 M. The fine-tuning of the energy transfer is achieved by changing the acid concentration of the solution. This important property of these systems is eminently suited for the construction of molecular switches.

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