J. Chem. Research (S),
2000, 360–361
J. Chem. Research (M),
2000, 0901–0930

Structure and photophysical properties of constrained donor-acceptor [2]catenanes bearing an appended secondary donor

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The synthesis of three donor–acceptor [2]catenanes are reported, along with their photophysical properties as measured using the technique of time-resolved transient absorption spectroscopy.

Construction of molecular architectures displaying attractive chemical and mechanical properties requires careful design criteria that permit the judicious positioning of responsive modules at well-defined positions and orientations.[1,2] A particularly aesthetic design motive concerns the interlocking of an electron-accepting *N,N'*-bipyridinium-based cyclophane with its complementary electron donor and this approach has been used extensively for the assembly of catenanes and rotaxanes.[8] These systems are especially attractive with regard to construction of photoactive devices since interaction between the donor and acceptor moieties causes the appearance of a charge-transfer (CT) absorption band in the visible region.[9] Direct illumination into this CT band promotes an electron from the HOMO of the donor to the LUMO of the nearby acceptor, thereby forming a radical ion pair (RIP) in unitary quantum yield.[10] Practical applications for these systems have been restricted by the realization that the rate of charge recombination occurs on the picosecond time scale such that absorbed photonic energy is rapidly converted into heat.[11] For certain [2]rotaxanes, however, it was demonstrated that electron transfer to a secondary donor could be made competitive with charge recombination provided the donor is correctly positioned.[12–13] We now report the possibility that improved systems might be engineered from the corresponding [2]catenanes since these latter species are more rigid and better defined in terms of local structure around the central donor-acceptor complex. Because the rate of electron transfer depends critically on both distance and the nature of interspersed material, we consider that, to allow their effective entry into the electron transfer cycle, secondary redox reagents must be appended very close to the *N,N'*-bipyridinium-based cyclophane.[14] Furthermore, it can be anticipated that charge recombination within the RIP will be very fast and, consequently, it becomes necessary to ensure that there is a reasonable thermodynamic driving force for the secondary electron-transfer step.[15] The synthesis of such functionalized [2]catenanes has not been reported before and, therefore, we have attempted to devise a synthetic strategy that permits close positioning of a secondary electron donor to the photoactive center. Interrogation of the system by ultrafast laser spectroscopy indicates that the appended donor plays a modest part in the electron-transfer events that follow from direct excitation into the CT absorption band.

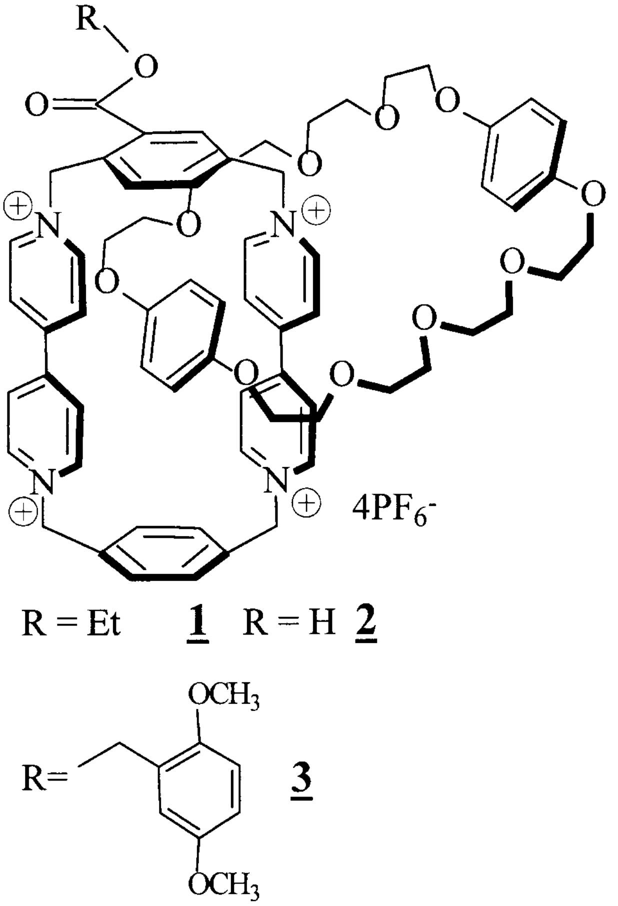

Fig. 1 Representation of the [2]catenanes used in this study.

The type of [2]catenanes used in this study are depicted in Figure 1. As part of the programme the properties of the catenanes have been studied using ^{1}H NMR, X-ray crystallography, electrochemistry and electronic absorption spectroscopy. The associative interaction between the donor-acceptor units that comprise the two interlocked rings of the [2]catenanes causes formation of a charge-transfer (CT) absorption band for which the maximum is slightly sensitive to structural variations. Illumination into this CT absorption band with a short laser pulse generates a compact radical ion pair (RIP), which for **1** and **2** survives for *ca.* 50 ps before undergoing charge recombination to restore the ground state. The rate of charge recombination can be rationalized in terms of the amount of energy that has to be dissipated among skeletal vibrational modes and is slower than that found for closely-related rotaxanes (Table 1).

In contrast, the charge recombination dynamics within the RIP formed from catenane **3**, are more complex and it is suggested that external dimethoxybenzene donor is involved in the overall process. A full rationalization of these results is presented in the full text version.

Techniques used: Sub-picosecond laser flash photolysis, cyclic voltammetry, ^{1}H NMR (variable temperature)

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Table 1 Thermodynamic and calculated parameters for donor–acceptor complexes

Compound	λ(eV)[a]	ΔG^{o} (eV)[b]	k_{CR} (10^{10} s^{-1})[c]
PQ/DMB[d]	0.74	2.31	5.6
Anth-rot[e]	0.50	2.05	7.1
1	0.58	2.05	2.0
2	0.58	2.06	1.8
3	0.57	2.05	1.4

[a] Total reorganization energy calculated using equation **(2)** from full text version.

[b] Free energy change for charge recombination.

[c] Calculated using $k_{CR} = 1/\tau_{CR}$

[d] Intermolecular charge-transfer complex formed between *N,N′*-dimethyl-4,4′-bipyridinium and 1,4-dimethoxybenzene (values taken from reference 15).

[e] [2]Rotaxane containing anthracene stoppers that π-stack to the viologen units of the cationic cyclophane (taken from ref. 13).

Schemes: 1

Figures: 9

We thank the EPSRC funded Mass Spectrometry Service at Swansea for analytical services. This work was supported by the Nuffield Foundation (ACB), Glasgow University and a grant from the Royal Society of London (AH). The award of a RSC JWT Jones Travel Fellowship (ACB) is also gratefully appreciated.

Received 22 March 2000; accepted 22 May 2000
Paper 00/231

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