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Digest Paper

Designing photoswitches for molecular solar thermal energy storage

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ABSTRACT

Solar energy conversion and solar energy storage are key challenges for a future society with limited access to fossil fuels. Certain compounds that undergo light-induced isomerisation to a metastable isomer can be used for storage of solar energy, so-called molecular solar thermal systems. Exposing the compound to sun light will generate a high energy photoisomer that can be stored. When energy is needed, the photoisomer can be catalytically converted back to the parent compound, releasing the excess energy as heat. This Letter gives examples of selected molecular solar thermal systems found in the literature. The focus of the Letter is on examples where molecular design has been used to improve the performance of the molecules, and as such it may serve as an inspiration for future design. The selected examples cover five widely studied systems, notably: anthracenes, stilbenes, azobenzenes, tetracarbonyl-fulvalene-diruthenium compounds and norbornadienes.

Contents

Introduction

Photoinduced isomerisation of organic molecules and organometallic compounds has been proposed as a possible way to store solar energy in the form of latent chemical bonds.[1–3] In these so-called molecular solar thermal systems (MOST), a parent photoisomer is irradiated by light and transformed into a high energy metastable photoisomer. The photoisomer can subsequently be converted back to the original parent compound by exposure to a catalyst or by heating. During the back conversion the photoisomer releases the stored energy in the form of heat. Several factors need to be optimised when designing a MOST system, including energy storage density, solar spectrum match (the ability of the molecule to absorb a large fraction of the solar spectrum), quantum yield of photoconversion, the half-life of the high energy isomer and thereby the height of the barrier for back conversion. To optimise all these factors at the same time in a single molecular system is a challenging task, yet an intriguing challenge. With this digest article we present examples of different attempts to optimise molecular systems towards MOST applications. Our examples include engineering of anthracenes (see section 'The anthracene system'), stilbenes (see section 'The stilbene system'), azobenzenes (see section 'The azobenzene system'), fulvalene-diruthenium compounds (see section 'The fulvalene diruthenium system') and norbornadienes (see section 'The norbornadiene system'). Our selection of examples is chosen to highlight how one can proceed in optimising the systems by chemical design.

The anthracene system

The photodimerisation of anthracene was suggested as a method to convert light into chemical energy as early as 1909.[4,5]

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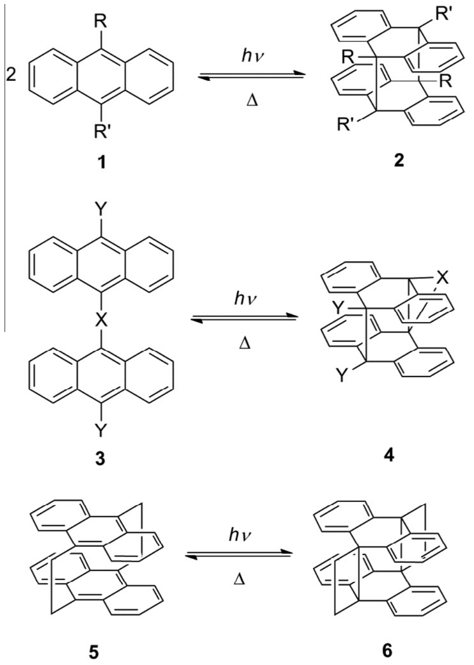


Figure 1. Photo-induced dimerisation of anthracene and cyclisation of linked anthracene dimers.

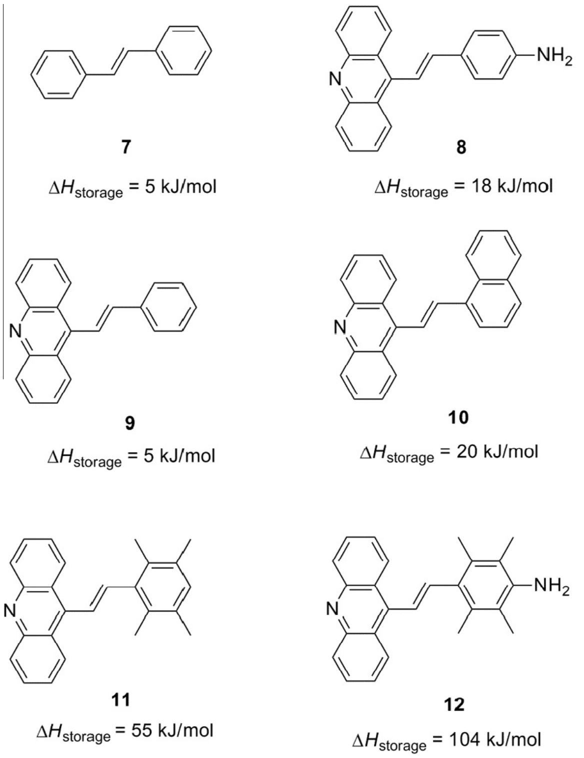


Figure 2. Structure and storage enthalpy of *E*–*Z* isomerisation of stilbene (**7**) and related compounds.

Anthracene is a rigid aromatic hydrocarbon, which dimerises via a [4+4] cycloaddition upon absorption of light at ca. 400 nm.[3,6] It then re-emits the stored energy as heat by thermal treatment or by irradiation with UV light (below 300 nm), thus conforming to established criteria for a MOST material.[7] The quantum efficiency (σ) for the forward reaction is concentration dependant, approaching 0.3 at high concentration, with a storage enthalpy ($\Delta H_{storage}$) of 65.2 kJ/mol.[6] By functionalising the anthracene monomer (**1**, Fig. 1) with donor and acceptor groups the enthalpy could be increased to 83.6 kJ/mol (R = H, R′ = CN), though the quantum efficiency remained concentration dependant.[8,9]

In order to increase the quantum efficiency and disassociate it from concentration, Jones et al. synthesised a range of linked anthracene dimers **3**–**6**.[6] Quantum efficiencies of up to 0.29 were achieved with the singly bridged system (**3**; X = CHOH, Y = H), and $\Delta H_{storage}$ was as high as 72.3 kJ/mol (for X = CH_2, Y = H). The highest quantum yield, however, was seen for the doubly bridged system at 0.36, though the storage enthalpy was reduced to 35.5 kJ/mol. In the case of the singly linked dimer, the four-membered ring produced when X = CH_2CH_2 leads to a greater $\Delta H_{storage}$ than the three-membered ring produced when X = CH_2 (72.3 and 61.0 kJ/mol, respectively).

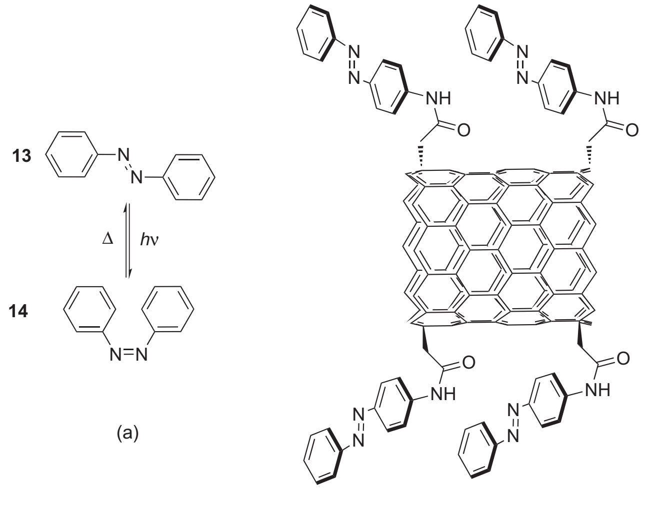
The stilbene system

Stilbenes (Fig. 2) are a class of organic compounds which undergo a *E*–*Z* photoisomerisation when exposed to light in the range 300–700 nm, making them interesting compounds with regard to solar energy storage since some derivatives absorb light well into the visible part of the solar spectrum. A major drawback, however, is the low storage enthalpy associated with this isomerisation, only 5 kJ/mol for unsubstituted stilbene, **7**.[10,11] Mancini and co-workers investigated the stilbene-like compounds 9-styrylacridines (**8**–**12**), and discovered that the storage enthalpy (also 5 kJ/mol for unsubstituted 9-styrylacridine) could be greatly increased by introducing different functional groups.[10,11] When one phenyl unit was functionalised with an electron donating amine group (**8**) the stored enthalpy increased four-fold, through increased electron delocalisation in the structure.[11] A similar effect was observed when the phenyl ring was replaced by a 1-naphthyl group (**10**), also furthering the conjugated system and thereby stabilising the *E* isomer, while the *Z* isomer is believed to be less affected due to its strained angular geometry and thereby limited π-conjugation.[11]

A further improvement on the storage enthalpy was achieved when the steric bulk about the phenyl moiety was increased through the addition of four methyl groups (2,3,5,6-tetramethylstyrylacridine, **11**).[10,11] The ortho methyl groups are believed to destabilise the *Z* isomer, thereby increasing the storage enthalpy to 55 kJ/mol. The highest enthalpy, however, was observed when the two above effects were combined in the tetramethyl-aminostyrylacridine, **12**. The increased delocalisation and steric hindrance have concomitant but opposing effects, lowering the energy of the *E* isomer while destabilising the *Z* isomer respectively, leading to a storage enthalpy of 104 kJ/mol (close to that of a chemical bond).[11]

The azobenzene system

Azobenzenes (Fig. 3), are among the most widely studied molecular photoswitches and have attracted recent attention in the field of molecular solar thermal storage. Azobenzenes absorb light in the visible range (absorption onset ca. 400 nm) and release heat upon re-isomerisation from *Z*–*E*.[2] Though these compounds drew attention in the 1980s as potential MOST systems, their low storage enthalpy (41.5 kJ/mol[12] for azobenzene; **13**) and low activation barrier to re-isomerisation ($t_{1/2}$ = ca. 4 days for **13**) lead to them being largely discounted.[12,13] Recent computational work, however, has prompted renewed interest in these systems.[14,15] Grossman and Kolpak performed a DFT study on azobenzene covalently bound to carbon nanotubes (CNTs). The CNTs acted as templates conferring a close-packed, ordered arrangement of molecules. The storage energy per azobenzene molecule increased by up to 30% compared to the free state, due to favourable interactions between close-packed molecules stabilising the *E* isomers relative



(a)

(b)

Figure 3. (a) Photoisomerisation of azobenzene. (b) Azobenzene functionalised CNT.

to the *Z*.[15] This increase, however, occurred with concomitant lowering of the activation energy for the back reaction. Further calculations suggested this could be overcome by hydroxyl functionalisation of the azobenzene molecules, inducing intra- and intermolecular hydrogen bonds in both *E* and *Z* isomers, such that a 260% increase in ΔH (up to 149.55 kJ/mol) and a 20% increase in the activation barrier for back conversion, E_A could be achieved (115.78 kJ/mol), relative to gas phase azobenzene (for which ΔH is calculated to be 56.93 kJ/mol and E_A 95.52 kJ/mol). The increased E_A is equivalent to a half-life of over a year. By varying CNT dimensions, azobenzene density and orientation, volumetric energy densities of up to 2.48 MJ/L (comparable to state of the art Li-ion batteries) might be feasible.[15]

Grossman and Kolpak extended their DFT study into other carbon-based templates (graphene, C_{60}, β-carotene, pentacene and alkenes), combined with functionalised azobenzene molecules (to enhance the spectral overlap with solar light and favourable packing interactions) and identified a range of potential candidates which possessed enhanced properties.[14] In this extensive study, inducing order in the various azobenzene derivatives led to increased energy density and E_A as well as electronic and optical properties.

Of the promising new MOST system candidates proposed by Grossman and Kolpak,[14,15] the unfunctionalised azobenzene/CNT hydrid material has now been synthesised.[16] Unfortunately the group was only able to achieve packing densities of azobenzene on the CNTs of 1/18.2 (compared to 1/8 which was modelled) due to a challenging experimental preparation. The energy density and activation energy were thus unchanged relative to free azobenzene because the molecules experienced no close-packing. However, condensing the hybrid materials in the solid state and allowing them to 'bundle' forced a close-packed arrangement in the material, doubling the storage energy (Fig. 4).[16]

Experimental groups have also investigated the properties of the proposed azobenzene/graphene hybrid materials with positive results.[17,18] Storage energy could be improved up to 269.8 kJ/mol as well as re-isomerisation activation energy and half-life (up to 225 days).[17] This was achieved by tuning the intra- and intermolecular H-bonding interactions with positioning of an electron withdrawing group (SO_3H) at either *para* or *ortho* on the unbound benzene moiety of the azobenzene molecule. The authors were able to achieve packing densities of up to 60% by weight (one azobenzene for every 11–12 carbon atoms on the graphene).

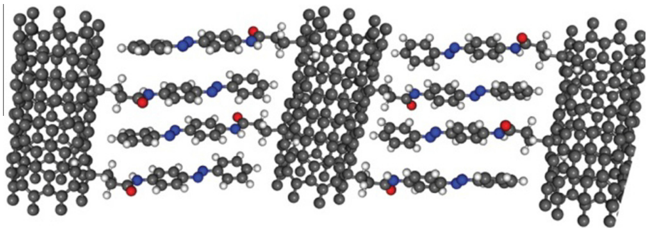
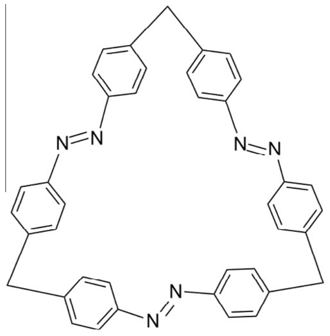


Figure 4. Illustration of azobenzene functionalised CNTs bundling in the solid state. [Adapted with permission from reference 16. Copyright (2014) Nature Publishing Group].

An alternative method to improve the properties of azobenzene for MOST systems has been proposed, which involves introducing macrocyclic ring strain rather than template induced interactions.[19] Computational modelling suggests molecular rings of linked molecules (e.g., compound **15**) can improve energy densities by imposing strain in the molecules. By varying the linker group, number of azobenzene monomer units, and the position and number of hydroxyl groups on the azobenzene rings (to induce H-bonding), with a calculated maximum energy density of 600 kJ/kg might be feasible. To date these compounds have not been reported experimentally and a future challenge for synthetic chemists might be to attempt this.



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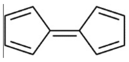
The fulvalene diruthenium system

Fulvalene, **16**, is a highly unstable compound that cannot be isolated. Since the 1960s, however, a considerable number of transition metal complexes have been reported having fulvalene-derived ligands.



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In 1983, Vollhardt and co-workers reported the synthesis of tetracarbonyl-fulvalene-diruthenium, **18**, from dihydrofulvalene, **17**, and triruthenium dodecacarbonyl (Fig. 5).[20,21] Earlier reports on fulvalene complexes relied on the coupling of cyclopentadienyl-metal complexes, while **18** was prepared from **17**, which is much more stable than **16**. Prepared by coupling of sodium cyclopentadienide with iodine, solutions can be stored under nitro-

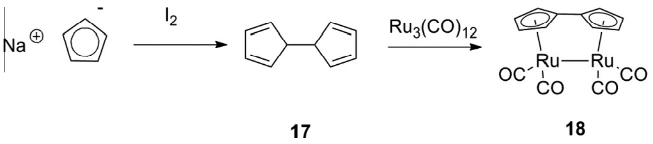
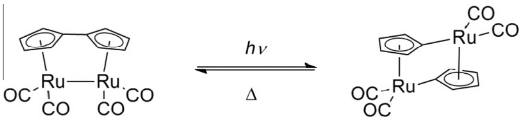
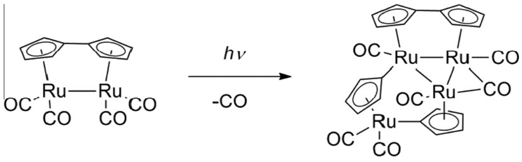


Figure 5. Synthesis of tetracarbonyl-fulvalene-diruthenium, **18**.



18 **19**

Figure 6. Reversible photoisomerisation of **18**.



18 **20**

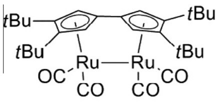
Figure 7. Formation of by-product **20** by UV-irradiation of **18**.

gen for hours at −78 °C. When added slowly to triruthenium dodecacarbonyl in refluxing 1,2-dimethoxyethane or xylenes, it gives **18**, which can be isolated as a yellow solid. Compound **18** can be handled in air, but degrades slowly in air over time.

In solution, **18** was found to undergo reversible photoisomerisation (Fig. 6) upon irradiation with visible light (**18** has an absorption onset of 470 nm).[20] The photoisomer, **19**, does not absorb in the visible region, and yellow solutions of **18** turn colourless upon irradiation, although a brown colour is often seen as a result of degradation. For instance, UV-light may cause irreversible loss of carbonyl ligands and formation of **20** (Fig. 7).[22]

The mechanism for the isomerisation of **18** was first believed to be concerted,[22] but was later shown to proceed via two short-lived intermediates (**21** and **22**; Fig. 8).[23,24] The Ru–Ru bond is broken first, and the over-all rate-limiting step for the isomerisation is the rotation around the Cp–Cp bond.

Compound **18** is robust in the absence of air and in contrast to stilbene or norbornadiene (see section 'The norbornadiene system'), it absorbs visible light. Still, **18** is not perfect for a MOST system; for instance, **18** and especially **19** are not very soluble in most solvents. Introduction of *tert*-butyl substituents (compound **23**), leads to an increased solubility, but at the expense of a rather complicated synthesis (five steps are required to prepare the 2,3-di-*tert*-butylcyclopenta-1,3-diene).[25] A more convenient way to increase the solubility was found in compounds **24** and **25**:[26] the corresponding dihydrofulvalene solution is prepared in a one-pot reaction, Figure 9. Two isomers of the product are obtained, and these are not easily separated, but were found to have identical photochemical properties. Using the **24**/**25** mixture, it was possible to demonstrate photoisomerisation and back conversion in a closed, small-scale solar-thermal reactor.[26] This principle has also been demonstrated combined with photon up-conversion, to increase the overall efficiency.[27] The idea of photon up-conversion is to merge two low-energy photons into one high-energy photon, and hence increase the fraction of the solar spectrum that can be utilised by the MOST system.



23

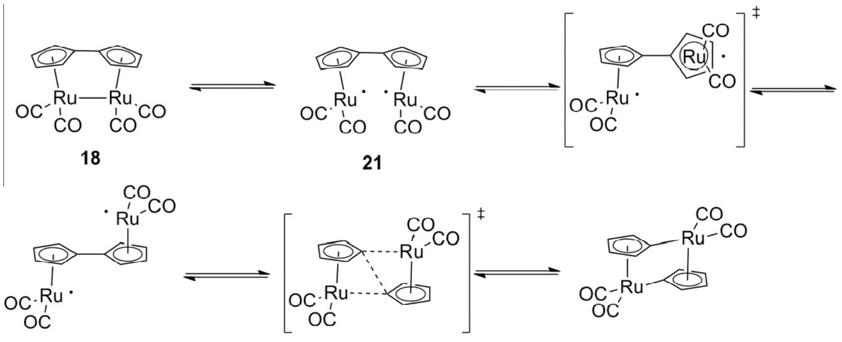
While aliphatic groups increase the solubility compared to **18**, perfluorinated alkane chains had the opposite effect and reduce the solubility significantly; a mixture of **26** and **27** (Fig. 10) was obtained in a similar manner as **24** and **25**.[28]

It is tempting to replace the expensive and heavy ruthenium atoms with iron, the lightest member of group 8 in the periodic table, but the iron analogue does not form any isolatable photoisomer.[25] The explanation is that irradiation of the diiron analogue of **18** gives a singlet *syn*-diradical (corresponding to **21**), which is too short-lived to undergo intersystem crossing to the triplet surface, where isomerisation occurs for ruthenium.[29] Going down group 8 and completing the story, also osmium forms an analogue to **18**; this compound does photoisomerise, but the isomerisation is irreversible.[25] An extensive study of fulvalene-dimetal compounds was recently published by Vollhardt and co-workers.[30]

The norbornadiene system

The norbornadiene system is the most widely studied MOST system to date, and the literature up to 2002 has been reviewed previously.[31,32] Deriving its name from the island of Borneo, since it shares the same core structure as natural products such as borneol, norbornadiene is not a natural product, but was first produced synthetically in the early 1950s; norbornadienes are now readily available through Diels–Alder reactions between cyclopentadienes and acetylenes. Norbornadiene's potential as a material for energy storage was not immediately obvious. For many years, however, chemists had struggled to synthesise compounds displaying the quadricyclane ring system. These attempts were unsuccessful until Cristol and Snell irradiated norbornadiene-2,3-dicarboxylic acid, **28**, with UV light;[33] this produced the corresponding quadricyclane dicarboxylic acid, **29**, through an intramolecular [2+2] cycloaddition (Fig. 11).

Quadricyclane itself (**31**) was first obtained by direct irradiation of norbornadiene, **30**[34] and, independently, in the presence of



18 **21** **22** **19**

Figure 8. Proposed mechanism for isomerisation of **18**.

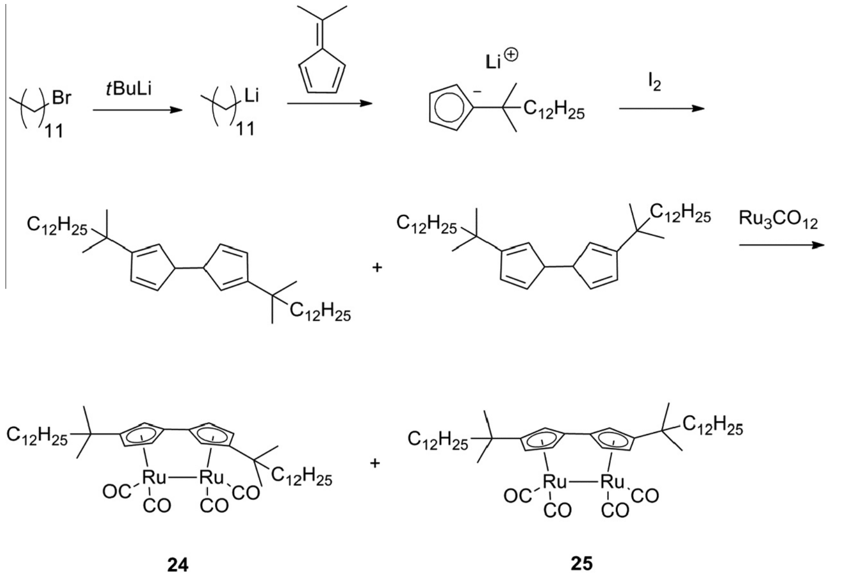


Figure 9. Synthesis of a more soluble mixture of compounds **24** and **25**.

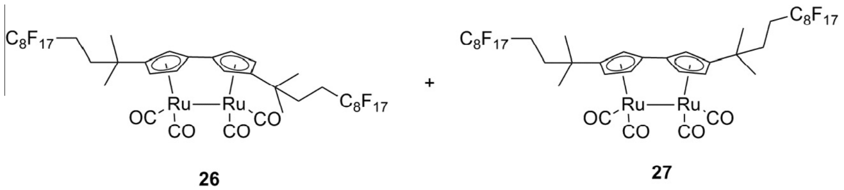


Figure 10. Perfluorinated analogues of **24** and **25** have low solubilities in organic solvents.

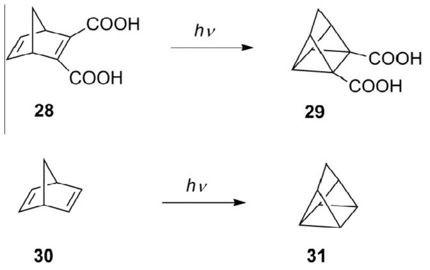


Figure 11. Photoisomerisation of norbornadiene-2,3-dicarboxylic acid (**28**) and norbornadiene (**30**).

triplet photosensitisers;[35] for synthetic purposes, the reaction is best performed using acetophenone as a sensitiser.[36] When irradiation was performed in the vapour phase, **30** was found to isomerise to toluene, or to decompose to cyclopentadiene and acetylene.[37]

The quadricyclane molecule is strained and thus stores a significant amount of energy ($\Delta H = 96$ kJ/mol), which can be released again since the norbornadiene—quadricyclane isomerisation is reversible. **30** is commercially available and has a low molecular weight; several effective catalysts have also been developed for the backward reaction.[31] On the other hand, **30** is prone to polymerisation, and may form explosive peroxides in the presence of air and light. **30** is a mobile liquid, which can easily be pumped through a device without the need to dilute it with solvent, but the volatility (boiling point 89 °C) and flammability may cause problems. Most importantly, however, **30** only absorbs UV light, and is not isomerised by sunlight to any extent. Hence, in order to become a useful MOST system, some improvements are necessary: the absorption must be red-shifted and the quantum yield increased without compromising the barrier of back-conversion.

The most successful strategy to red-shift the absorption of norbornadiene is to introduce one or two electron withdrawing, or one electron withdrawing and one electron donating group at one of the C=C double bonds. Two aromatic substituents at the same double bond create a large conjugated system which is broken upon isomerisation, thus ensuring a blue shifted absorption of the corresponding quadricyclane. Apart from red-shifting the absorption, introduction of substituents at the C=C double bond typically also leads to a significant increase in quantum yield.[32]

Some early attempts to modify the spectroscopic properties of norbornadiene by this approach include compounds having one aryl- and one aroyl substituent, leading to an absorption onset of up to 400 nm.[38] If one aryl and one imine substituent was introduced, the corresponding quadricyclane was obtained in protic solvents, while isomerisation at the C=N double bond occurred in aprotic solvents.[39] Norbornadienes like **32** (Fig. 12) were found to absorb up to 460 nm, but some of the derivatives prepared did not give full conversion, but led to photostationary equilibrium mixtures. Derivatives of **32** are relatively straight forward to pre-

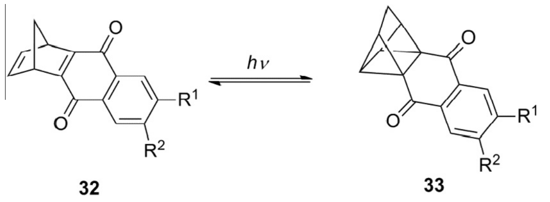


Figure 12. R^1 and R^2 is H, Me or OMe.

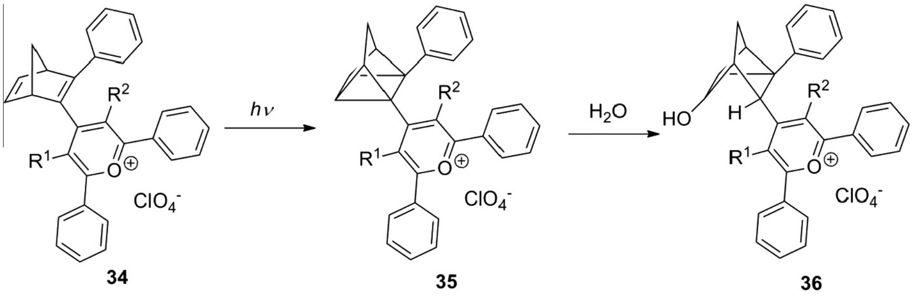
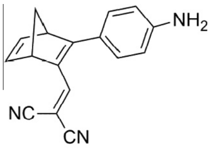


Figure 13. In the presence of traces of moisture, **34** is irreversibly transformed to **36**.

pare by Diels–Alder reactions between cyclopentadiene and naphtoquinones.

Norbornadienes bearing cationic heterocyclic substituents may have absorption onset up to 580 nm,[40] well into the green area of the spectrum, and close to the optimal absorption for a MOST system of ca. 600 nm.[41] Unfortunately, these systems are not suited for practical use due to establishment of equilibria between the norbornadiene and the quadricyclane, or due to competing side reactions: although **34** rapidly isomerises even in diffuse light, the corresponding quadricyclane, **35**, is easily degraded by traces of moister (Fig. 13).[40]

An even stronger bathochromic shift was observed for compound **37**, with an absorption onset of 620 nm, corresponding to orange light.[42] The quantum yield for that particular compound was 0.1, smaller than those for other similar compounds reported in same study.



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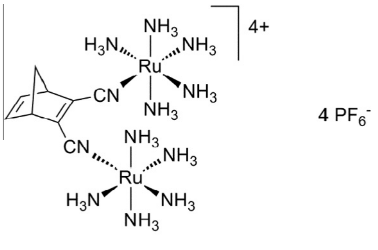
A record 700 nm absorption onset was observed upon coordination of Ru(II) to 2,3-dicyanonorbornadiene.[43] Unfortunately, the quantum yield of **38** is only 8.3×10^{-4} at 500 nm.



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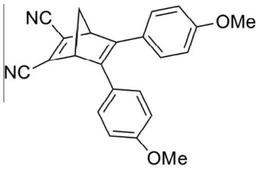
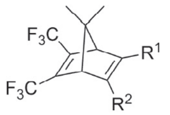
An alternative strategy is to introduce electron withdrawing and electron donating groups at the two different C=C double bonds, since this gives rise to charge transfer bands in the absorption spectrum. One of the more efficient systems, **39**, has an absorption onset of 557 nm.[7] High quantum yields were retained when the compounds were included in thin poly-methyl methacrylate films.[44]



39

A problem that has frequently been encountered is too low activation energy for the reverse reaction, which makes the metastable quadricyclanes too labile to be stored for any practical length of time. Introducing methyl substituents on the bridge head, and trifluoromethyl groups on one of the double bonds has been shown to improve the life-time of the quadricyclane.[45]



40-41

40: R^1 = *p*-$Me_2NC_6H_4$- and R^2 = *p*-$MeOC_6H_4$-. **41**: R^1 and R^2 = 2-benzofuranyl

As an example, **40** has an absorption onset of 510 nm and a half-life of the corresponding quadricyclane of 1.1 years. Compound **40** unfortunately showed a comparable rapid degradation upon repeated photoisomerisation/back-conversion. By contrast, **41** showed excellent cyclability. Absorption onset for **41** was 480 nm, and the half-life of the quadricyclane was 72 h. This demonstrates the difficulty to optimise all important parameters

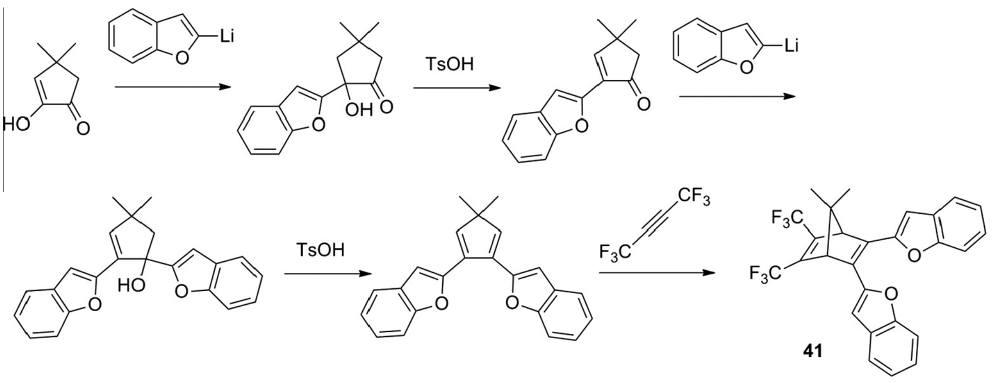


Figure 14. Synthesis of **41** through a Diels–Alder approach.

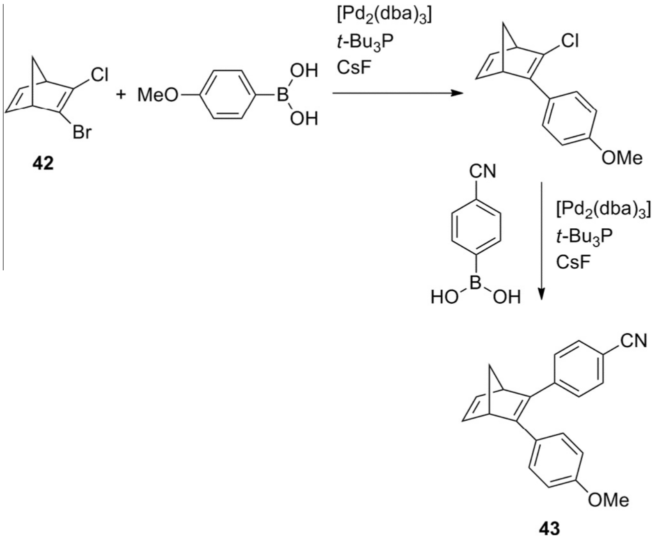
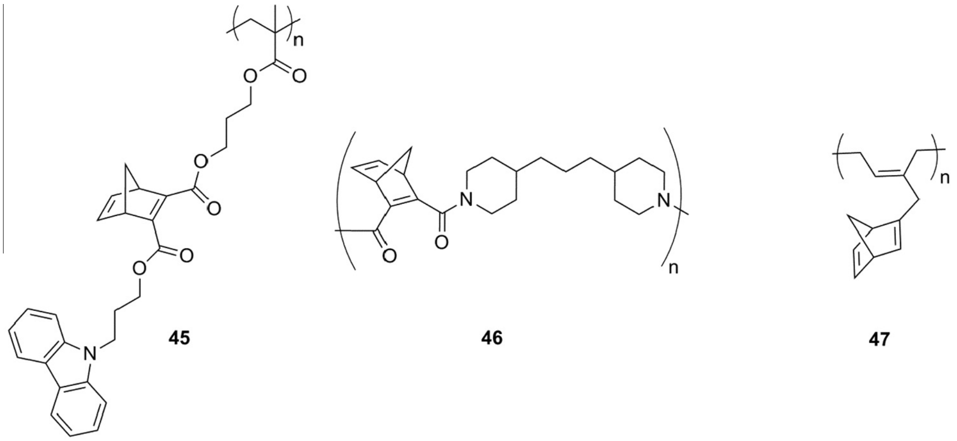


Figure 15. Synthesis of **43** from **42** by Suzuki cross coupling.

simultaneously. The compounds in this study were prepared from substituted cyclopentadienes and hexafluoro-2-butyne through a Diels–Alder reaction, Figure 14.[45]



Polymers **45**, **46** and **47**.

A recent report from our laboratory shows the same well-known trend in decreased half-life of the quadricyclane as the absorption of the norbornadiene is red-shifted.[46] Inspired by Tam[47] and co-workers, we prepared 2,3-substituted norbornadienes, for example, **43,** via Suzuki cross-coupling, Figure 15, rather than the more common Diels–Alder approach. Starting from 2-bromo-3-chloro-norbornadiene, **42**, the two different sites at the C=C bond can be addressed individually, reducing the risk of introducing two identical aryl groups. The second step is performed at elevated temperature. Figures 15 and 16 therefore serve as illustrating examples for the two main routes to 2,3-substituted norbornadienes.

Introducing heavy substituents on norbornadiene increases the molecular weight, and thus reduces the storage capacity in terms of Jg^{-1}. Linking norbornadiene moieties together, will help to compensate for that effect. The linked norbornadienes **44a**–**c** displayed in Figure 16 underwent photoisomerisation in two steps, with absorption onsets up to 560 nm.[48]

A different strategy to improve the photoisomerisation of norbornadiene is to introduce charge transfer through coordination of metal atoms to the norbornadiene π-system. Norbornadiene readily forms coordination compounds with a variety of metal atoms (there are currently over 400 crystal structures of such compounds) but only copper (I) compounds have been effective. These experiments are closely related to the development of photosensitisers for increasing the quantum yield for isomerisation of norbornadiene, and will not be discussed further in this Letter.

Norbornadiene moieties have also been included in polymer structures, which tend to prevent undesired side reactions upon irradiation. For convenience of synthesis, the polymers are often polyesters (e.g., **45**[49]) or polyamides (e.g., **46**[50]) prepared from norbornadiene-2,3-dicarboxylic acids, or norbornadiene-2-carboxylic acids, but norbornadiene has also been connected to a polyisoprene backbone in a heteroatom-free polymer, **47**.[51] Norbornadiene may be a part of the polymer chain itself, or be linked to the polymer as a side arm. Photosensitisers such as carbazole[49] or benzophenones[52] may also be attached to the polymer to facilitate the photoisomerisation.

Outlook

A century after the discovery of anthracene as a medium for storage of solar energy, new potential MOST systems continue to be introduced. Two examples are given here. Rhodopsin is a retinal protein responsible for the perception of light via a photon-induced *cis*–*trans* alkene isomerisation.[53] Recently, Sampedro and co-workers have investigated retinal-like compounds as potential MOST systems (Fig. 17).[54] Compounds **48a**–**d** undergo an *E*–*Z* isomerisation upon absorption of light at approximately 300 nm, a reaction which can be reversed thermally (though room temperature is sufficient for this process).[2,54] The authors were able to red-shift the parent isomer absorption by tuning the R-group (R = Ph, p-MeOPh, p-NO$_2$Ph, 2-naphthyl) extending the conjugation in the molecule, and in a second strategy, protonation of the imine nitrogen atom led to greater activation energies for the back reac-

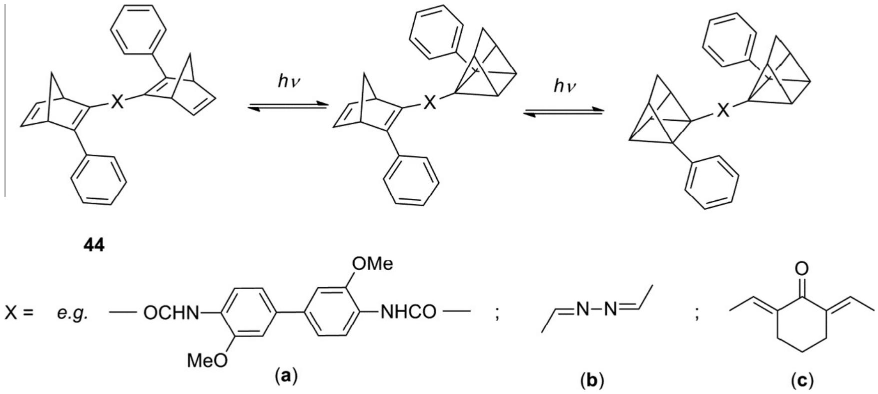


Figure 16. Two-step photoisomerisation of linked norbornadienes.

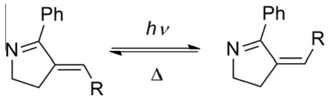
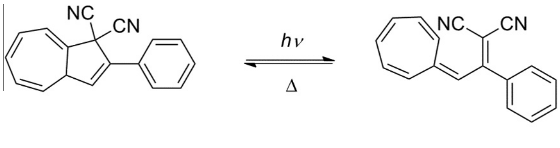


Figure 17. Photoisomerisation of retinal-like molecules. R = Ph (**48a**), *p*-MeOPh (**48b**), *p*-NO_2Ph (**48c**) and 2-naphthyl (**48d**).



50 **51**

Figure 18. Photoisomerisation of photoswitch **50**.

tion (these derivatives were stable for at least 6 days at room temperature, only reverting to the parent isomer when heated to 60 °C).[54]

Recently, Brønsted Nielsen and co-workers, synthesised and investigated the dihydroazulene (DHA; **50**)–vinylheptafulvene (VHF; **51**) photoswitch (Fig. 18).[55] Thus far the compound cannot store sufficient energy to be considered for MOST systems, but with some future design work, this system has considerable potential. In conclusion, there are both much room for improvement on the existing systems and possibilities to find new systems. Especially, engineering the systems to achieve a high quantum yield for visible light and still have a long half-life of the photoisomer and a low molecular weight is, as pointed out in this review, a great challenge.

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