Providing power for miniaturized medical implants: triplet sensitization of semiconductor surfaces

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Here, we recognize the growing significance of miniaturized devices as medical diagnostic tools and highlight the need to provide a convenient means of powering such instruments when implanted into the body. One of the most promising approaches to this end involves using a light-collection facility to absorb incident white light and transfer the photonic energy to a tiny semiconductor embedded on the device. Although fluorescent organic molecules offer strong potential as modules for such solar collectors, we emphasize the promise offered by transition metal complexes. Thus, an extended series of binuclear Ru(II)/Os(II) poly(pyridine) complexes has been shown to be highly promising sensitizers for amorphous silicon solar cells. These materials absorb a high fraction of visible light while the Ru(II)-based units possess triplet energies that are comparable to those of the naphthalene-based bridge. The metal complex injects a triplet exciton into the bridge and this, in turn, is trapped by the Os(II)-based terminal. The result is extremely efficacious triplet-energy transfer; at room temperature the rate of energy transfer is independent of distance over some 6 nm and only weakly dependent on temperature.

1. Introduction

In contemporary healthcare, self-diagnostic technologies that can be used at home are set to replace costly visits to and by the doctor. Heavy, unwieldy medical equipment that until now has been wheeled laboriously around hospital floors is being transformed into portable...
machinery that can be used at home or in a remote village. Tiny implants that can test, diagnose and even alert doctors to problems with their patients will replace routine visits that are often disruptive and time consuming. Medical devices incorporating miniaturized electronics are at the stage of provoking a radical rethink of chronic illness and disability treatment. Electronic appliances combining digital and analogue circuitry, sophisticated power sources, high reliability and extremely compact dimensions can—or soon will—perform a diverse variety of medical tasks [1]. These tasks range from the mundane timing of medication doses to the complex restoration of basic senses for patients unable to tend to themselves. These miniaturization processes are responsible for numerous critical medical advancements, and are intended to restore the patient’s personal dignity. Because so much of the body’s operation is electrical in nature, nervous response, sensory input and muscle control are all potential areas for treatment, enhancement or replacement using miniaturized electronics [2].

One well-known example of the progress and expectations associated with the introduction of electronic implants is the development of an artificial heart [3]. However, the field is much wider than this and many new treatments and health aids now under development take advantage of implanted miniaturized electronics. The diversity of these technologies is reflected in the results of a simple search on the Internet for terms such as ‘artificial vision’ and ‘implant’. Each returns hundreds of matches that outline technologies and therapies available now or at the trial stage.

Several teams of researchers are working on methods to restore sight by some kind of electronic circuitry. There are two general approaches to this problem; the best method for each patient will depend on the particular cause of blindness. The simplest treatment [4] involves implanting a small semiconductor disc behind the eye, directly over the nerve ganglia at the rear of the retina. This disc functions as an artificial retina; light hitting the surface causes generation of electrical stimuli that are applied to the optic nerve and restore some degree of vision. The semiconductor is powered by the incident daylight, or indirectly by an external light built into the frame of heavy-duty spectacles and trained in the direction of the disc. A second prototype [5] has the semiconductor disc fitted into the lens tissue and sends electrical impulses to the brain using the existing optical chains. Partial vision can be restored in certain cases, but without the appreciation of colour.

Another concept that relies on miniaturized electronics is the bio-electronic neuromuscular implant. Such devices [6] are used to restore muscular activity through the application of electrical impulses to strategic locations in affected muscles. These implants have broad implications in cardiac assistance, neural control and improved prosthesis operation. A hearing aid is yet another type of implant that takes advantage of advanced miniaturized electronics. Cochlear implants operate by delivering electrical stimulation directly to auditory nerves in the inner ear in response to external sounds [7]. A portion of the equipment is implanted behind the ear and wired to electrodes inserted into the cochlea. The other equipment includes a miniaturized microphone and audio processor that amplifies, filters and digitizes sound waves. These enhanced sound waves are then transmitted to the implant and electrodes electromagnetically or through a wired connection.

Implanted medical devices are made possible, in part, through the miniaturization of increasingly sophisticated electronic circuits. Many components are now reduced to the size of sand grains and require robotic equipment for their assembly. The elimination of extraneous interconnect wiring is also an invaluable advance. As a result, circuits are able to operate at high speed and to maintain a regular temperature without overheating. A key requirement for any long-term electronic implant, especially in terms of minimizing the possible risk of infection, is the elimination of wires running from the outside world into the device. Medical electronic hardware is usually battery powered, but batteries ultimately need to be replaced. Not all implants have power sources that are easy to substitute and this simple realization has fuelled interest in the generation of implanted electronic devices making use of rechargeable power systems. While not as effective as a wired connection, this technique can operate without any physical connection between the power source and the implant. Typically, the power requirement lies in the range of 1.5–2.0 eV and, although far from the only solution, this seems an ideal opportunity to develop...
new forms of light-activated photovoltaic systems as the charging mechanism. Here, we consider
the case for using transition metal poly(pyridine) complexes as artificial light absorbers but, by
way of introducing the subject, we refer firstly to organic dyes because this particular field has
advanced much further.

2. Artificial light-harvesting systems

The concept behind the application of artificial light-harvesting arrays stems from Nature, where
many disparate organisms use a network of pigments to absorb incident sunlight and channel the
excitation energy to a receptor where chemical reactions are initiated. This basic concept is used in
such processes as DNA repair [8], vision [9], photosynthesis [10], phototrophic bacteria [11] and
light-adapted proteins [12]. The need for some kind of light-collection facility is obvious when the
organism lives in a dark atmosphere, perhaps deep in the ocean, but is less striking for normal
environments. However, it should be realized that many of the chemical processes used by Nature
to bring about its multifarious functions are difficult to achieve and the actual choice of reagents
is highly restricted. It adds a tremendous burden onto these reagents if they also have to absorb
light of a particular frequency, or more likely over a certain range of frequencies, to such a point
that it becomes improbable to identify appropriate materials. Deselecting the two options—light
collection and catalytic performance—solves the main problem and allows optimum compounds
to be used for each purpose. A remaining problem, however, is that the two processes have to be
coupled together at some point so that the harvested photons are directed to the site where the
chemistry will occur. This is not a trivial problem because light causes catastrophic problems if
left unchecked, most notably by sensitizing production of singlet molecular oxygen. Thus, light
collection, itself quite easy to engineer, must be allied to excitation energy transfer (EET) from
the initial chromophore to a suitable energy acceptor that will initiate the desired reactions. The
requirements for efficient electronic energy transfer are themselves quite demanding.

Over the past decade or so, we have produced a range of organic-based artificial arrays that
display intramolecular EET between disparate pigments arranged in a logical sequence by way of
covalent linkages [13]. Most of these networks have been built around boron dipyrromethene
(Bodipy) dyes, which are especially versatile modules with which to assemble complex, multi-
component structures. One example of such an artificial array is illustrated in figure 1. Here,
there is a gradient of excited-state energy levels degrading from pyrene (labelled PYR on figure 1)
to the conventional Bodipy dye (labelled BOD on figure 1) and finally to the π-expanded Bodipy
dye (labelled EXBOD on figure 1). Photons collected by PYR, which absorbs and fluoresces in the
near-UV region, are transferred quantitatively to BOD. The latter, which is a highly stable dye,
possesses a strong absorption band centred at around 510 nm and emits strongly at about 525 nm.
In fact, BOD transfers its excitation energy to the appended EXBOD with an efficiency that is in
excess of 90 per cent [14]. The expanded dye absorbs and emits in the far-red region and is an
effective sensitizer for many different types of solar cell. In this way, the absorption spectrum of
EXBOD is augmented by the spectral profiles of the ancillary chromophores such that a much
greater fraction of the solar spectrum is collected by the array than by any of the individual dyes.

A large variety of such arrays have been synthesized over the years [15] and the dynamics
of intramolecular EET have been studied by steady-state and time-resolved fluorescence
spectroscopy. These dyes have been designed with a linear gradient of excitation energy levels
in mind, although alternative design elements are possible [16]. Perhaps the most elaborate array
produced to date is that illustrated in figure 2. This network comprises a total of 21 chromophores
arranged in a rational way that channels photons to the terminal EXBOD unit with very high
efficiency. Related research has used fullerenes decorated with disparate Bodipy dyes [17] and
examined different types of spacer group [18]. The direction of EET along the molecular axis can
be switched by rapid protonation of the terminal acceptor using a photo-acid [19]. The mechanism
of the EET process has been resolved in many cases, while the relative contributions of coulombic
EET and electron exchange have been delineated by high-pressure techniques [20]. The molecular
arrays are readily dispersed in plastic films without harm to the overall EET efficacy.
Cast films of the polymer-embedded dye have been shown to operate as effective sensitizers for several different types of semiconductor, including amorphous silicon. Of course, the organic materials are not cheap because of the synthetic chemistry involved in manufacture of the arrays. Nonetheless, they function as highly effective light-collection facilities and prove that such strategies are efficacious. A genuine advantage of this approach is that the array can be tuned to the optical output of the excitation source, whether this be solar, laser, light-emitting diode, pulsed or white light. The organic dyes are non-toxic and alleviate the need to use a large surface area semiconductor. Plastic films produced in this way are inconspicuous and can
be built into many different devices. There are real benefits from developing covalent arrays of logically arranged dyes, rather than relying on surface adsorption of a cocktail of isolated dyes. Also, discrete liquid crystalline materials [21] can be assembled in situ that function in much the same fashion. Thus, considerable progress has been made with organic dyes that operate via the excited-singlet state, and we now turn attention to the corresponding triplet-excited-state processes. Because Bodipy dyes are resistant to triplet formation, we have used transition metal (notably ruthenium(II)-based) poly(pyridine) complexes as alternative sensitizers.

3. Triplet sensitizers

Ruthenium(II) and osmium(II) poly(pyridine) complexes are valuable triplet sensitizers, often forming relatively long-lived excited-triplet states in quantitative yield under illumination with visible light. An advantage to be gained by using such chromophores in place of organic dyes is that the metal complexes tend to possess broad absorption spectral profiles that stretch out towards 750 nm and thereby offer an enormous range of putative excitation wavelengths. Prior work has shown [22] that certain ruthenium(II) tris(2,2′-bipyridine) complexes function as useful sensitizers for silicon solar cells but the field is still in its infancy. These latter complexes offer the benefit of a long-lived triplet state, typically this being several µs at room temperature, but do not favour the construction of linear arrays. Instead, we have opted to use the corresponding ruthenium(II) bis(2,2′:6′,2′-terpyridine) complexes as the starting point for our work [23]. Unfortunately, while solving the construction problem this approach is flawed in as much as the resultant triplet-excited state is short lived, being in the region of 250 ps in fluid solution at ambient temperature. A further problem with these complexes is that their photophysical properties tend to be heavily dependent on temperature [24] because of the availability of numerous excited states situated at slightly higher energies. This particular issue is important when making mechanistic considerations.

The lifetime problem can be overcome by attaching an ethyne group at the 4′-position of the ligand. This simple approach [25] lowers the energy of the corresponding metal-to-ligand charge transfer (MLCT) triplet state because of its electron-withdrawing character, thereby decoupling the MLCT triplet from upper-lying excited states. Additionally, electron delocalization takes place at the triplet level and this inhibits mixing with the upper states. The net result is that mononuclear ruthenium(II) bis(2,2′:6′,2′-terpyridine) complexes bearing a single 4′-ethynylated residue possess triplet lifetimes of the order of 50 ns or so [26], whereas it is not unusual to observe [27] triplet lifetimes of several µs for binuclear complexes linked via oligo(ethylene) bridges. We have opted to use such binuclear complexes. Related work with ethynylated osmium(II) bis(2,2′:6′,2′-terpyridine) complexes has led to the identification of systems displaying triplet lifetimes in the region of some hundreds of nanoseconds under ambient conditions [28].

A small level of refinement has been the addition of naphthyl groups in the highly conjugated bridging unit. This strategy introduces a bridge-centred (BC) excited-triplet state into the congested triplet manifold [29]. Now, the BC excited-triplet state retains a triplet energy that is not too dissimilar to that of the terminal MLCT triplet state, as was demonstrated by consideration of the isolated bridging ligands [30]. The actual triplet energy of the BC excited-triplet state depends weakly on the number of naphthyl units accreted into the bridge, the energy decreasing progressively with each added naphthyl unit. In this way, the BC triplet can be positioned above or below that of the terminal MLCT triplet, at least in the case of the ruthenium(II) bis(2,2′:6′,2′-terpyridine) complexes. The final complexes, therefore, are as shown in figure 3. These compounds are readily soluble in polar organic solvents, unlike the isolated ligands, and moderately luminescent in solution at room temperature.

4. Synthesis and characterization

Full details regarding synthesis and characterization of these complexes will be published in a more specialized journal. Solvents were purchased as spectroscopic grade and were stored over...
appropriate drying agents. Butyronitrile was distilled immediately before use. Photophysical properties for the isolated bridges have been published [30].

5. Photophysical properties of the homotopic metal complexes

Initial attention focused on the luminescence properties of the binuclear osmium(II) complexes (see figure 3 for structures) in butyronitrile (BuCN) at 77 K. In each case, the absorption and excitation spectra match very well over the entire visible spectral region. Time-resolved emission studies indicated that the decay profile was mono-exponential for all complexes while the emission peaks were found at about 13 000 cm$^{-1}$. Under these conditions, it was observed that the emission lifetime remained at about 1.35 µs in all cases and, therefore, is independent of the length of the bridging ligand. As expected, the absorption and emission spectral profiles are dominated by transitions considered to be characteristic of the osmium(II) complex [29]. Furthermore, the radiative rate constants ($k_{\text{RAD}} = 9.0 \times 10^3$ s$^{-1}$) derived from the emission yields and lifetimes are too high to be associated with the BC triplet state but are fully consistent with those expected for the metal complex [28]. It is considered, therefore, that the BC triplet states are too high in energy to reside in thermal equilibrium with triplet states localized on the terminal osmium(II) complex. Instead, photons absorbed by the BC excited-triplet state are transferred quantitatively to one of the terminal complexes as demonstrated by comparing absorption and excitation spectra.

Attention now turns to the corresponding ruthenium(II) complexes where the triplet MLCT state associated with the metal complex lies at much higher energy than is found with the osmium(II) complexes. Thus, the MLCT absorption transition associated with the metal complex is centred at around 500 nm, irrespective of the length of the bridge, whereas weak emission is seen in the far-red region in BuCN at 77 K. As above, there is excellent agreement between absorption and excitation spectra (figure 4), while the luminescence peak ($E_{00}$) is located at about 14 400 cm$^{-1}$ in each case (table 1). Time-resolved emission profiles are mono-exponential (figure 5) at long times and allow determination of the triplet lifetimes ($\tau_L$) in the absence of molecular oxygen. The derived values are collected in table 1 and are seen to increase systematically with increasing length of the bridging ligand. At the same time, there is a progressive decrease in the emission quantum yields ($\Phi_L$) measured under the same conditions (table 1). The total reorganization energy ($\lambda_T$) associated with decay of the triplet state, as determined by spectral curve fitting routines [29], is insensitive to the length of the bridging ligand (table 1). The implication here is that only the triplet MLCT state emits under these conditions. Examination of the decay profiles on shorter time scales indicates that, in each case, there is a fast component that depletes the MLCT triplet state (figure 5). This situation is entirely consistent with the emissive MLCT triplet state being in thermal equilibrium with a non-emissive BC triplet state [30]. As such, the fast component refers to setting up the equilibrium, whereas the slower component refers to decay
Figure 4. Overlaid absorption (solid curve) and excitation (dotted curve) spectra recorded for one of the binuclear Ru(II) complexes in BuCN solution at room temperature. (Online version in colour.)

Table 1. Summary of the photophysical properties recorded for the binuclear ruthenium(II) complexes in a butyronitrile glass at 77 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_0$ (cm$^{-1}$)</th>
<th>$\Phi_L$</th>
<th>$\tau_L$ (μs)</th>
<th>$\alpha$</th>
<th>$\lambda_T$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuN1Ru</td>
<td>14 390</td>
<td>0.067</td>
<td>9.3</td>
<td>0.84</td>
<td>400</td>
</tr>
<tr>
<td>RuN2Ru</td>
<td>14 380</td>
<td>0.050</td>
<td>17.2</td>
<td>0.63</td>
<td>430</td>
</tr>
<tr>
<td>RuN3Ru</td>
<td>14 390</td>
<td>0.036</td>
<td>29.2</td>
<td>0.15</td>
<td>440</td>
</tr>
<tr>
<td>RuN4Ru</td>
<td>14 400</td>
<td>0.021</td>
<td>35.7</td>
<td>0.074</td>
<td>410</td>
</tr>
<tr>
<td>RuN5Ru</td>
<td>14 390</td>
<td>0.013</td>
<td>40.5</td>
<td>0.040</td>
<td>450</td>
</tr>
<tr>
<td>RuN6Ru</td>
<td>14 390</td>
<td>0.010</td>
<td>44.6</td>
<td>0.028</td>
<td>440</td>
</tr>
</tbody>
</table>

*Refers to the peak of the first vibronic component derived by curve fitting the emission spectrum to a series of Gaussian profiles.

of the thermal equilibrium [31]. These derived lifetimes can be used to determine the fraction ($\alpha$) of triplet MLCT present at equilibrium (table 1) and it is seen that this is a relatively high value. However, it is notable that $\alpha$ decreases steadily with increasing length of the bridging ligand.

This latter situation demands that the triplet states associated with MLCT and BC triplets are close in energy, with the energy of the former being independent of the length of the bridge. The energy of the triplet state resident on the BC excited-triplet state decreases slightly with increasing length [30]. From the derived $\alpha$ values, it is clear that the MLCT state is at lower energy than the BC triplet for short bridges but the triplet BC state becomes lower in energy as the length increases. Comparable behaviour is observed for the corresponding mononuclear ruthenium(II) complexes, where the triplet MLCT state lies at higher energy than found for the corresponding binuclear complexes. Overall, this gives a relatively large database by which to confirm the general situation. Using the entire dataset, and extracting rate constants for energy transfer ($k_{TT}$) from the triplet MLCT state to the BC excited-triplet state indicates that the rate depends on the size of the energy gap between these two triplet states (table 2), exactly in accord with the Marcus theory [32]. Thus, the system seems to be reasonably well understood in terms of this simple scheme.

6. Photophysical properties of the Ru(II)/Os(II) mixed-metal complexes

The Ru(II)/Os(II) mixed-metal complexes possess interesting absorption spectra in the sense that there is strong absorption across the entire visible spectrum until about 740 nm (figure 6). Related, but much simpler, binuclear complexes have been used by many researchers [33–35] as a means
Figure 5. (a) Time-resolved luminescence decay profile recorded for Ru–NAP$_3$–Ru in BuCN at 77 K. The inset shows a semi-logarithmic trace. (b) The corresponding traces recorded on a shorter time scale for Ru–NAP$_2$–Ru and Ru–NAP$_4$–Ru. The inset shows decay traces for Ru–NAP$_3$–Ru and for the control compound. The fast component refers to setting up the thermal equilibrium while the slow component represents deactivation of the equilibrium mixture of triplet states. (Online version in colour.)

Table 2. Summary of the parameters that characterize triplet-energy transfer along the bridge in the various Ru(II)/Os(II) binuclear complexes in a butyronitrile glass at 77 K.

<table>
<thead>
<tr>
<th>compound</th>
<th>$\tau_1$ ($\mu$s)$^a$</th>
<th>$\tau_{Ru}$ (ns)$^b$</th>
<th>$\tau_{Os}$ (ns)$^c$</th>
<th>$k_{DB}$ ($10^8$ s$^{-1}$)</th>
<th>$k_{BD}$ ($10^8$ s$^{-1}$)</th>
<th>$k_{BA}$ ($10^8$ s$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>RuN$_1$O</td>
<td>1.28</td>
<td>10.8</td>
<td>11.9</td>
<td>1.2</td>
<td>6.4</td>
<td>—</td>
</tr>
<tr>
<td>RuN$_2$O</td>
<td>1.34</td>
<td>20.1</td>
<td>27.3</td>
<td>2.2</td>
<td>3.7</td>
<td>13.1</td>
</tr>
<tr>
<td>RuN$_3$O</td>
<td>1.37</td>
<td>3.6</td>
<td>27.1</td>
<td>6.4</td>
<td>1.2</td>
<td>16.1</td>
</tr>
<tr>
<td>RuN$_4$O</td>
<td>1.30</td>
<td>2.0</td>
<td>42.5</td>
<td>9.1</td>
<td>0.73</td>
<td>19.0</td>
</tr>
<tr>
<td>RuN$_5$O</td>
<td>1.36</td>
<td>1.5</td>
<td>63.4</td>
<td>11.7</td>
<td>0.50</td>
<td>18.0</td>
</tr>
<tr>
<td>RuN$_6$O</td>
<td>1.37</td>
<td>1.2</td>
<td>88.7</td>
<td>13.4</td>
<td>0.40</td>
<td>18.0</td>
</tr>
</tbody>
</table>

$^a$Emission lifetime recorded for the Os(II)-based terminal following direct excitation into that unit.

$^b$Emission lifetime recorded for the Ru(II)-based terminal following preferential excitation into that unit.

$^c$Lifetime corresponding to the growth of the Os(II)-based emission following preferential excitation into the Ru(II)-based terminal.
by which to study long-range electron exchange between the metal centres. We might expect similar behaviour for the naphthyl-bridged systems described here. Indeed, the luminescence spectra recorded in BuCN at 77 K show emission from the Os(II) centre following excitation into the spin-forbidden MLCT transition associated with this chromophore. The lifetime and quantum yield, these being insensitive to changes in the length of the bridging ligand, remain in very good agreement with those reported earlier for the binuclear osmium(II) complexes. The presence of a Ru(II)-based terminal, therefore, has no effect on the photophysical properties of the Os(II)-based terminal.

Excitation of these Ru(II)/Os(II) mixed-metal complexes at 490 nm, where the Ru(II)-based chromophore is the dominant but not only absorber, leads to luminescence from the Os(II)-based emitter. There is only a minor amount of emission that can be assigned to the Ru(II)-based emitter (figure 7). Furthermore, the excitation and absorption spectra match very well over the relevant wavelength range and provide strong support for the notion of intramolecular triplet energy transfer across the bridge. Additional support for this claim comes from time-resolved emission studies in which the triplet lifetime for the Ru(II)-based terminal (τ_Ru) is seen to decrease as the bridge becomes longer (table 2). At the same time, emission from the opposite terminal grows-in after the excitation pulse by first-order kinetics. The corresponding lifetime (τ_Os) for this process increases significantly as the bridge becomes longer (table 2). The only logical explanation for this situation is that the Ru(II)-based donor injects triplet excitation energy into the bridge, as outlined above, while the corresponding Os(II)-based terminal acts as an energy sink for the resultant wave packet. In order for this system to operate, it is necessary for the BC triplet state to be localized on a single naphthalene unit such that the triplet exciton hops along the bridge in an incoherent manner until trapped by the acceptor. Incidentally, there is an approximate semi-logarithmic relationship between the inverse of τ_Os and the number of naphthalene units in the bridge.

Within the confines of this model, simulation of the experimental decay curves allows a crude estimation of the various rate constants associated with end-to-end triplet-energy transfer (table 2). In particular, the simulations allow determination of the rate constants for reversible energy transfer between the Ru(II)-based donor and the first naphthalene unit in the bridge. The ratio of these (forward and reverse) rate constants is fixed by the respective energy gap, according to the Boltzmann law, but the actual values are derived from the fit. Now, it becomes possible to obtain rate constants (k_DB) for exciton injection into the bridge and for the reverse step (k_BD) for each member of the series. The trend is as might be expected in that k_DB increases as the energy gap decreases. The simulations also permit estimation of the rate constant (k_BA) for triplet-energy
Figure 7. Luminescence spectra recorded for Ru–(NAP)$_3$–Os in BuCN at either 77 K or room temperature (RT) as indicated, following preferential excitation into the Ru(II) complex. The spectral profile is dominated by emission from the Os(II) complex. The inset shows an amplification of the RT spectrum, with the individual contributions labelled. (Online version in colour.)

Table 3. Summary of the parameters that characterize triplet-energy transfer across the bridge in the various Ru(II)/Os(II) binuclear complexes in butyronitrile at room temperature.

<table>
<thead>
<tr>
<th>compound</th>
<th>$R_{DA}$ (Å)$^a$</th>
<th>$k_{EET}$ ($10^{10}$ s$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuN$_1$O</td>
<td>19.8</td>
<td>1.3</td>
</tr>
<tr>
<td>RuN$_2$O</td>
<td>27.9</td>
<td>2.2</td>
</tr>
<tr>
<td>RuN$_3$O</td>
<td>36.0</td>
<td>2.8</td>
</tr>
<tr>
<td>RuN$_4$O</td>
<td>44.1</td>
<td>2.4</td>
</tr>
<tr>
<td>RuN$_5$O</td>
<td>52.2</td>
<td>2.3</td>
</tr>
<tr>
<td>RuN$_6$O</td>
<td>60.3</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$^a$Distance between the edges of the donor and acceptor units as determined from molecular mechanics calculations.

$^b$Rate constant for long-range triplet-energy transfer following preferential excitation into the Ru(II)-based terminal.

transfer from the bridge to the Os(II)-based acceptor. In fact, these values are fairly constant across the series (table 2). The final piece of information that can be extracted from these simulations is the rate constant for triplet-energy transfer between adjacent naphthalene residues. The average time needed for the exciton to jump between neighbours is about 10 ns at 77 K. This is a crude estimate but nonetheless highly informative.

In BuCN at room temperature, it is not possible to resolve emission for the Ru(II)-based donor from the background but the lifetime of this excited-triplet state can be determined from transient absorption spectral measurements. In this case, there is no obvious growth for the time-resolved emission signal associated with the corresponding Os(II)-based acceptor. This latter finding can be used to suggest that the rate-limiting step under these conditions relates to triplet exciton injection into the bridge. The derived rate constants ($k_{EET}$) for end-to-end triplet-energy transfer are collected in table 3, together with the edge-to-edge separation distances ($R_{DA}$) measured from molecular mechanics calculations. It is remarkable to find only a weak dependence of the rate on separation distance as shown by figure 8. In fact, the rate is slightly faster at a separation of 60 Å than at 20 Å. Of course, it has to be realized that the energetics of the bridge vary along the series so a simple comparison is not meaningful [32].
Figure 8. Effect of edge-to-edge separation distance ($R_{DA}$) on the rate constant for end-to-end triplet-energy transfer along the molecular axis, as measured for the mixed-metal complexes. The dots refer to the experimental values determined in BuCN at room temperature. The solid curve is a non-linear fit to the Marcus theory.

7. Sensitization studies

Prior work has established that ruthenium(II) tris(2,2’-bipyridine) complexes can transfer triplet excitation energy to silicon quantum dots under illumination with visible light [22]. To achieve contact between the quantum dot and sensitizer, the latter was anchored to the silicon surface via a short hydrocarbon chain. There is, however, sufficient flexibility for the reactants to come into orbital contact during the triplet lifetime. The energy-transfer mechanism, therefore, most likely involves close-range electron exchange. It is interesting to note that there is no obvious sign of intermolecular interactions between the surface-bound sensitizer and this situation is markedly different from what happens at reasonably high loading of organic-based sensitizers. Here, the planar aromatic cores tend to self-associate [12] in the form of dimers and excimers and these effects not only complicate the transfer mechanism but also introduce severe inefficiencies. The absence of aggregation for the metal complexes, together with their improved light-harvesting properties, provides the main justification for the present work.

Our initial studies in this area used a mononuclear ruthenium(II) complex as a sensitizer for gold nanoparticles (refer to figure 3 for structure; $n = 3$). Here, a solution of the metal complex in acetone was added to an aqueous suspension of the Au nanoparticles under sonication. The excess acetone was removed by purging with a stream on N$_2$ gas, whereas the metal complex was attached to the Au surface, presumably via the vacant terpyridine ligand [36]. The final suspension was stable for several days but ultimately aggregated into clumps that caused light scattering. As is well established, the maximum for the plasmon absorption band for Au nanoparticles depends on the diameter because of quantum confinement. With 20 nm diameter particles, the peak maximum lies at about 520 nm and closely overlaps absorption by the MLCT state localized on the metal complex. Triplet-energy transfer occurs but is relatively ineffective, as judged by steady-state emission studies. For larger Au nanoparticles, the absorption band moves towards the red; for 100 nm diameter particles the peak maximum occurs at 610 nm. This wavelength overlaps strongly with luminescence from the mononuclear metal complex and, in this case, triplet-energy transfer is quantitative.

Related studies used flexible amorphous silicon sheets as the basic substrate. Here, the binuclear ruthenium(II) complexes (see figure 3 for structures; $n = 2, 3$ and 4) were dispersed in CHCl$_3$ containing poly(methylmethacrylate) and spin coated onto the Si sheet. Under direct illumination into the MLCT absorption band, it was not possible to observe luminescence from the metal complex at either room temperature or 77 K. At the same time, current was generated in the Si sheet as long as the light was turned on. The strong implication is that the metal
complex transfers excitation energy to the semiconductor. Aggregation does not occur, even at high loadings of metal complex. The same situation was found with the mixed-metal binuclear complexes (see figure 3 for structures; n = 2 and 4) where luminescence from the Os(II)-based centre was extinguished when the compound is coated onto the semiconductor surface. Again it was confirmed by way of an action spectrum that triplet-energy transfer to Si produces the required photocurrent. With small surface areas, there is a definition increase in current generation by depositing the metal complex as a polymer film, although this crude approach is far from optimal.

8. Concluding remarks

It has been shown that, with proper selection of the bridge, almost distance-independent triplet-energy transfer can be achieved over separations of ca 60 Å; this is among the longest distances yet reported for triplet-energy transfer. Even at 77 K, the probability of end-to-end energy transfer exceeds 95 per cent and the rate increases substantially at higher temperatures. The key feature of this system is that the individual units that combine to form the bridge are only weakly coupled in electronic terms, as discussed for the isolated ligands [30], despite the presence of highly conjugated covalent connections. This poor electronic communication at the triplet level serves to isolate triplet excitons on individual naphthalene residues so that triplet-energy transfer along the bridge is an incoherent hopping process. Photons collected directly by the bridge are transferred to one of the terminals but eventually become trapped at the Os(II)-based unit, which functions as an effective sensitizer for silicon solar cells. The mixed-metal binuclear complexes collect photons over a wide spectral range and are extremely stable under prolonged illumination, in marked contrast to most organic-based light-collection arrays. In this respect, and allowing for the relatively straightforward synthesis, these materials are superior to the elaborate organic systems. It remains for strategies to be devised that attach the dye directly to the semiconductor surface via the Os(II)-based acceptor.

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