Energy transfer from rhenium(I) complexes to covalently attached anthracenes and phenanthrenes

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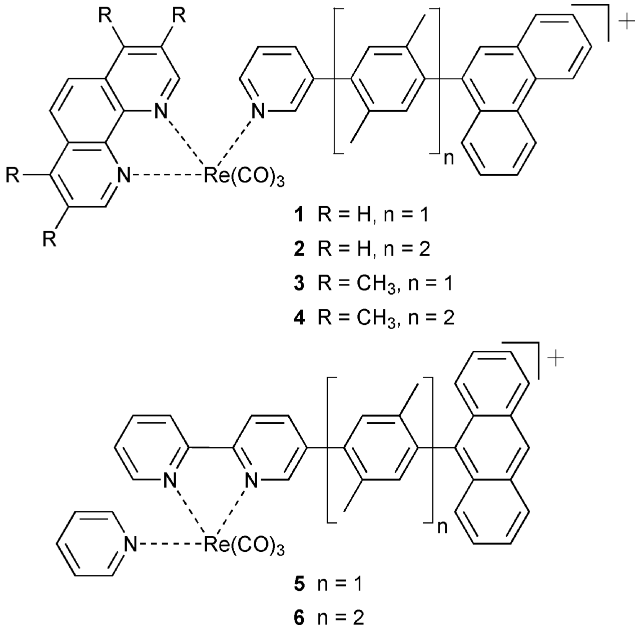
The synthesis and photophysical properties of a series of chromophore–quencher complexes are reported. They are all comprised of a luminescent rhenium(I) tricarbonyl diimine complex that is covalently attached to anthracene or phenanthrene moieties *via* rigid rod-like *p*-xylene bridges of variable lengths. Rhenium-to-anthracene energy transfer is strongly exergonic ($-\Delta G^0 \approx 0.9$ eV) and causes very efficient rhenium MLCT luminescence quenching. By contrast, rhenium-to-phenanthrene energy transfer is only observed when complexes with sufficiently high MLCT energies are used because for these dyads, the driving force for energy transfer is low ($-\Delta G^0 \approx 0.1$ eV). For a ~15 Å donor–acceptor distance, the rate constants of the weakly and the strongly exergonic energy transfer processes differ by more than 3 orders of magnitude.

Introduction

Energy transfer is a key process in photosynthesis and has therefore received much attention over the past few decades.[1] A wealth of theoretical and experimental studies has provided remarkably detailed insight into the subject of energy transfer.[2] In inorganic photochemistry, ruthenium(II) tris-bipyridine ($Ru(bpy)_3^{2+}$) type complexes have been used frequently to investigate triplet–triplet energy transfer.[3] In a particularly insightful study, it was shown that energy transfer from a $Ru(bpy)_3^{2+}$ donor to an $Os(bpy)_3^{2+}$ acceptor through covalent oligo-*p*-phenylene spacers takes place *via* a Dexter mechanism,[4] thereby supporting prior studies that have noted similarities between Dexter-type *energy* transfer and super-exchange *electron* transfer.[5] Rhenium(I) tricarbonyl diimines have also received significant attention regarding both electron and energy transfer processes.[6,7] Investigations of such rhenium complexes are among the few experimental studies that provide direct evidence for the so-called inverted driving force effect for energy transfer,[8] a phenomenon that is now rather well documented for electron transfer.[9] These complexes posses the following favourable properties: (i) their synthesis is facile,[10] (ii) they have relatively high lying MLCT excited states (>2.5 eV) that emit light,[10–12] (iii) the energies of these emissive states are tuneable through ligand variations,[11–13] and (iv) these MLCT states have lifetimes of the order of 0.5–10 µs,[12] thereby making long distance energy (and electron) transfer investigations possible.

Despite the enormous advances made in energy transfer research in recent years, there remain open questions, particularly regarding the factors that control energy transfer rates over long distances (>10 Å). Recent independently performed studies report on remarkably different distance dependencies for energy transfer through covalent oligo-*p*-phenylene–ethynylene bridges.[14,15] It appears plausible that these discrepancies are due to differences in donor–bridge energy gaps,[16] particularly in light of other recent theoretical and experimental studies.[17] A systematic investigation of this important issue asks for donor–bridge–acceptor systems, in which (i) energy transfer is competitive with other excited-state deactivation processes, (ii) the donor–bridge energy gap is independent upon the length of the bridge, and (iii) donor–bridge energy gap effects can be isolated from driving force (*i.e.* donor–acceptor energy gap) effects. The goal of the present study was to identify simple molecular systems that fulfil these requirements. Toward this end, we have synthesized and investigated the six dyads shown in Scheme 1. They are comprised of a rhenium(I) tricarbonyl diimine energy donor, *p*-xylene bridges, and a phenanthrene or anthracene energy acceptor.



Scheme 1

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Experimental

General information

Unless stated otherwise, all chemicals are commercial reagents and were used as supplied. All reactions and manipulations were carried out under an inert nitrogen atmosphere using standard (Schlenk) techniques. Solvents for synthesis were dried using drying columns where appropriate. Column chromatography, for product purification, was performed using silica gel from the Fluka chemical company (product no. 60745). ^{1}H NMR spectra were measured on a Bruker Avance 400 MHz spectrometer. All chemical shifts were determined from their relative displacements to partially deuterated solvent peaks and are reported relative to the tetramethylsilane signal. High-resolution mass spectra were measured on a QSTAR XL (AB/MDS Sciex) spectrometer whereby the samples were dissolved in methanol or CH_2Cl_2.

Optical absorption spectra were measured on a Cary 5000 spectrophotometer from Varian, and steady-state luminescence spectra were acquired using a Horiba Fluorolog-3 instrument. Time-resolved luminescence and transient absorption experiments were performed on the setup of Prof. A. Hauser, Department of Physical Chemistry, University of Geneva. This setup has been described recently in ref. 18. For all the optical spectroscopic measurements, dichloromethane of spectrophotometric grade (Sigma-Aldrich product no. 154792) was used. For the time-resolved studies, samples were deoxygenated by three subsequent freeze–pump–thaw cycles using appropriate home-built quartz cuvettes.

General synthetic procedure for lithiation reactions

The following procedure was applied for all borylation, stannylation, and trimethylsilylation reactions.[19] Typically, 1 g of bromoarene was dissolved in 25 mL anhydrous tetrahydrofuran (THF) and cooled to −78 °C in a dry ice–acetone bath. After 30 min, 1.1 equivalents of *n*-butyllithium solution (1.6 M in hexanes) were added dropwise *via* a syringe. After stirring for 60–120 min at −78 °C, 1.1 equivalents of the appropriate electrophile were added dropwise: triisopropylborate for borylation, tri-*n*-butyltin chloride for stannylation, and trimethylsilyl chloride for trimethylsilylation. Then, the solutions/suspensions were allowed to warm to room temperature over night. Work-ups usually included addition of water to the THF solution (in the case of borylation a 2 M aqueous hydrochloric acid solution to hydrolyze the boronic esters), followed by extraction of the crude products with several portions of dichloromethane. The crude products were purified by column chromatography (or in the case of the boronic acids by recrystallization). For the synthesis of 5-(tri-*n*-butyltin)-2,2′-bipyridine (**19**), the use of diethylether rather than tetrahydrofuran turned out to be indispensable.

General synthetic procedure for Suzuki-type C–C couplings

In a typical procedure, 1 g of bromo- or iodoarene was dissolved in 10 mL toluene or THF along with 1.1 equivalents of boronic acid. After the addition of 10 mL of 2 M aqueous Na_2CO_3 solution, the biphasic mixture was deoxygenated by bubbling nitrogen gas through it for 15 min. Between 1 and 10 mol% of $Pd(Ph_3)_4$ (Ph = phenyl) catalyst were then added, and the reaction mixture was refluxed over night. In some cases, refluxing had to be continued for up to 3 d. Work-up included extraction with dichloromethane, drying ($MgSO_4$), and evaporation of the organic solvent phase. The crude products were purified by column chromatography.

Procedure for the Stille-type C–C coupling

1 g of iodoarene and 1.2 equivalents of 5-(tri-*n*-butyltin)-2,2′-bipyridine (**19**) were dissolved or suspended together in 12 mL *m*-xylene. After deoxygenating by bubbling with nitrogen gas for 15 min, 20 mol% of $Pd(Ph_3)_4$ was added, and the reaction mixture was refluxed for 5 d. The solvent was subsequently evaporated under reduced pressure, and the residue was subjected directly to column chromatography. Yields were typically of the order of 20%; the use of other solvents (THF, toluene) or catalysts ($Pd(Ph_3)_2Cl_2$) led to even poorer results.

General procedure for rhenium complexation

For dyads **1**–**4** the method described in ref. 10 was followed (with the slight modification that silver triflate, rather than silver perchlorate was used). For dyads **5** and **6**, 300 mg of free ligand **20** or **23** were reacted with 1 equivalent of $Re(CO)_5Cl$ in 10 mL toluene at reflux for 5 h.[10,20] Solvent evaporation yielded the chloro complexes in almost quantitative yields. These were subsequently reacted with a 5-fold excess of pyridine in toluene in the presence of silver triflate to yield the target complexes. The triflate salts of all the final rhenium complexes were purified by column chromatography whereby a dichloromethane–methanol (98 : 2) eluent mixture was used. Complexation yields ranged from 25–85%.

Product characterization data

All ^{1}H NMR data were recorded on the 400 MHz spectrometer indicated above. The solvent was always $CDCl_3$, and all chemical shifts are given relative to the tetramethylsilane signal. Coupling constants, *J* are reported in Hz. The following abbreviations were used to designate the protons: An = anthracene, bpy = 2,2′-bipyridine, Me = methyl, Pe = phenanthrene, phen = 1,10-phenanthroline, py = pyridine, TMS = trimethylsilyl, xy = xylene.

Pe–xy–TMS 9. Obtained in 95% yield using the general Suzuki coupling methodology. Purified on silica using pentane as an eluent. δ_H/ppm: 0.47 (9H, s, TMS), 2.10 (3H, s, Me), 2.54 (3H, s, Me), 7.19 (1H, s, xy), 7.49 (1H, s, xy), 7.55 (2H, m, Pe), 7.62 (1H, d, Pe, *J* = 8.2 Hz), 7.67 (1H, s, Pe), 7.70 (2H, m, Pe), 7.92 (1H, d, Pe, *J* = 7.7 Hz), 8.79 (1H, d, Pe, *J* = 8.3 Hz), 8.82 (1H, d, Pe, *J* = 8.3 Hz).

Pe–xy–I 10. Obtained in quantitative yield from **9** using a TMS–halogen exchange method.[25] δ_H/ppm: 2.01 (3H, s, Me), 2.48 (3H, s, Me), 7.22 (1H, s, xy), 7.53 (2H, m, Pe), 7.60 (1H, s, Pe), 7.68 (3H, m, Pe), 7.85 (1H, s, xy), 7.90 (1H, d, Pe, *J* = 8.0 Hz), 8.76 (1H, d, Pe, *J* = 8.3 Hz), 8.79 (1H, d, Pe, *J* = 8.5 Hz).

Pe–xy–py 12. Synthesized from **10** and **11** following the general Suzuki coupling method. Purified on silica using a dichloromethane–methanol eluent mixture. The isolated yield was 20%. δ_H/ppm 2.10 (3H, s, Me), 2.34 (3H, s, Me), 7.24 (1H, s, xy), 7.31 (1H, s, xy), 7.57 (2H, br, Pe), 7.57 (1H, dd, py, *J* = 1.6, 6.0 Hz), 7.63 (1H, dd, Pe, *J* = 12.0, 1.2 Hz), 7.68 (1H, s, Pe), 7.68 (1H, dd, Pe, J = 7.6, 1.2 Hz), 7.72 (1H, dd, py, J = 8.2, 1.6 Hz), 7.73 (1H, dd, Pe, J = 12.0, 1.6 Hz), 7.93 (1H, dd, Pe, J = 7.6, 1.2 Hz), 8.69 (1H, dd, py, J = 5.0, 1.6 Hz), 8.78 (1H, d, Pe, J = 4.8 Hz), 8.79 (1H, d, Pe, J = 4.8 Hz), 8.82 (1H, d, py, J = 8.2 Hz).

[Re(phen)(CO)$_3$(Pe–xy–py)]$^+$ 1. Synthesized in 25% yield from Re(phen)(CO)$_3$Cl and free ligand **12** following the general rhenium complexation method. δ_H/ppm: 2.00 (3H, s, xy), 2.05 (3H, s, xy), 6.88 (1H, s, xy), 7.25 (1H, s, xy), 7.54 (1H, dd, Pe, J = 6.4, 1.6 Hz), 7.55 (1H, s, xy), 7.57 (2H, dd, Pe, J = 7.6, 1.6 Hz), 7.63 (1H, s, py), 7.68 (1H, dd, Pe, J = 7.6, 1.2), 7.72 (2H, dd, Pe, J = 8.2, 1.6 Hz), 7.82 (1H, d, py, J = 8.2 Hz), 7.91 (1H, dd, Pe, J = 7.6, 1.6 Hz), 8.13 (1H, dd, py, J = 5.6, 0.8 Hz), 8.23 (2H, m, phen), 8.29 (2H, s, phen), 8.49 (1H, d, py, J = 1.9 Hz), 8.78 (1H, d, Pe, J = 8.2 Hz), 8.81 (1H, d, Pe, J = 8.2 Hz), 8.93 (2H, d, phen, J = 8.2 Hz), 9.62 (2H, d, phen, J = 5.2 Hz). ESI-MS: *m*/*z* observed 810.1751 (M$^+$), expected 810.1761.

[Re(Me$_4$phen)(CO)$_3$(Pe–xy–py)]$^+$ 3. Synthesized in 45% yield from Re(Me$_4$phen)(CO)$_3$Cl and free ligand **12** following the general rhenium complexation method. δ_H/ppm: 2.07 (3H, s, Me–xy), 2.11 (3H, s, Me–xy), 2.76 (6H, d, Me–phen, J = 2.8 Hz), 2.94 (6H, s, Me–phen), 6.95 (1H, s, xy), 7.58 (1H, dd, py, J = 4.0, 0.8 Hz), 7.60 (2H, d, Pe, J = 6.0 Hz), 7.65 (1H, s, xy), 7.68 (3H, m, Pe), 7.72 (1H, dd, py, J = 8.8, 0.8 Hz), 7.73 (1H, dd, Pe, J = 8.0, 1.2 Hz), 7.79 (1H, d, py, J = 4.0 Hz), 7.84 (1H, dd, Pe, J = 8.0, 1.2 Hz), 8.39 (2H, s, phen), 8.68 (1H, d, py, J = 2.0 Hz), 8.78 (1H, d, Pe, J = 8.4 Hz), 8.82 (1H, d, Pe, J = 8.4 Hz), 9.20 (2H, d, phen, J = 1.6 Hz). ESI-MS: *m*/*z* observed 866.2356 (M$^+$), expected 866.2387.

Pe–xy$_2$–TMS 13. Obtained from reaction of **8** and **10** according to the general Suzuki coupling procedure in 75% yield. Purified on silica using pentane as an eluent. δ_H/ppm: 0.40 (9H, s, TMS), 2.50 (3H, s, Me), 2.13 (3H, s, Me), 2.20 (3H, m, Me), 2.05 (3H, m, Me), 7.07 (1H, m, xy), 7.11 (1H, d, xy, J = 5.6 Hz), 7.23 (1H, d, xy, J = 5.6 Hz), 7.40 (1H, d, xy, J = 4.2 Hz), 7.56 (1H, dd, Pe, J = 7.0, 1.2 Hz), 7.64 (1H, dd, Pe, J = 8.4, 1.2 Hz), 7.68 (2H, m, Pe), 7.71 (1H, s, Pe), 7.71 (1H, dd, Pe, J = 6.6, 1.2 Hz), 7.93 (1H, dd, Pe, J = 8.0, 1.2 Hz), 8.78 (1H, d, Pe, J = 8.0 Hz), 8.81 (1H, d, Pe, J = 8.4 Hz).

Pe–xy$_2$–I 14. Obtained in quantitative yield from **13** following a TMS–halogen exchange method.[25] δ_H/ppm: 2.02 (3H, s, Me), 2.08 (3H, s, Me), 2.12 (3H, m, Me), 2.45 (3H, m, Me), 7.04 (H, d, xy, J = 5.6 Hz), 7.11 (1H, m, xy), 7.20 (1H, m, xy), 7.53 (1H, m, Pe), 7.61 (2H, m, Pe), 7.67 (2H, m, Pe), 7.67 (1H, s, Pe), 7.77 (1H, m, xy), 7.90 (1H, dd, Pe, J = 7.6, 0.8 Hz), 8.75 (1H, d, Pe, J = 8.4 Hz), 8.79 (1H, d, Pe, J = 8.4 Hz).

Pe–xy$_2$–py 15. Synthesized from **11** and **14** according to the general Suzuki coupling method. Product purification occurred on silica with a dichloromethane–methanol mixture as an eluent. The yield was 35%. δ_H/ppm: 2.08 (3H, s, Me), 2.18 (3H, s, Me), 2.24 (3H, m, Me), 2.34 (3H, m, Me), 7.16 (1H, d, xy, J 5.6 Hz), 7.20 (1H, m, xy), 7.22 (1H, m, xy), 7.26 (1H, d, xy, J = 5.6 Hz), 7.44 (1H, dd, Pe, J = 8.8, 4.8 Hz), 7.58 (1H, m, py, J = 6.8, 1.2 Hz), 7.65 (2H, m, Pe), 7.71 (2H, m, Pe), 7.73 (1H, s, Pe), 7.81 (1H, m, py, J = 6.8, 1.6 Hz), 7.94 (1H, dd, Pe, J = 7.6, 1.2 Hz), 8.65 (1H, dd, py, J = 4.8, 1.6 Hz), 8.73 (1H, d, py, J = 1.6 Hz), 8.79 (1H, d, Pe, J = 8.4 Hz), 8.82 (1H, d, Pe, J = 8.4 Hz).

[Re(phen)(CO)$_3$(Pe–xy$_2$–py)]$^+$ 2. Synthesized from Re(phen)(CO)$_3$Cl and free ligand **15** following the general rhenium complexation method in 85% yield. δ_H/ppm: 2.01 (3H, m, Me), 2.07 (3H, s, Me), 2.15 (3H, s, Me), 2.19 (3H, m, Me), 6.83 (1H, m, xy), 7.09 (1H, d, xy, J = 5.6 Hz), 7.18 (1H, m, xy), 7.26 (1H, d, xy, J = 5.6 Hz), 7.50 (1H, dd, Pe, J = 7.6, 5.6 Hz), 7.59 (1H, dd, py, J = 7.2, 1.6 Hz), 7.63 (1H, m, Pe), 7.71 (3H, m, Pe), 7.71 (1H, s, Pe), 7.79 (1H, m, py, J = 7.2, 5.6 Hz), 7.93 (1H, dd, Pe, J = 7.6, 0.8 Hz), 8.10 (1H, d, py, J = 1.6 Hz), 8.22 (1H, d, phen, J = 5.2 Hz), 8.24 (1H, d, phen, J = 5.2 Hz), 8.31 (2H, s, phen), 8.46 (1H, s, py), 8.79 (1H, d, Pe, J = 8.6 Hz), 8.82 (1H, d, Pe, J = 8.6 Hz), 8.84 (2H, d, phen, J = 8.2 Hz), 9.61 (2H, d, phen, J = 4.8 Hz). ESI-MS: *m*/*z* observed 914.2390 (M$^+$), expected 914.2387.

[Re(Me$_4$phen)(CO)$_3$(Pe–xy$_2$–py)]$^+$ 4. Synthesized from Re(Me$_4$phen)(CO)$_3$Cl and free ligand **15** following the general rhenium complexation method in 25% yield. δ_H/ppm: 2.08 (3H, s, Me–xy), 2.11 (3H, s, Me–xy), 2.18 (3H, d, Me–xy, J = 13.4 Hz), 2.21 (3H, d, Me–xy, J = 13.4 Hz), 2.76 (6H, s, Me–phen), 2.94 (6H, s, Me–phen), 6.90 (1H, m, xy), 7.12 (1H, d, xy, J = 5.6 Hz), 7.21 (1H, d, xy), 7.27 (1H, d, xy, J = 5.6 Hz), 7.56 (1H, dd, Pe, J = 6.0, 3.6 Hz), 7.59 (1H, m, py, J = 7.2, 1.6 Hz), 7.65 (1H, m, Pe), 7.70 (3H, m, Pe), 7.72 (1H, s, Pe), 7.79 (1H, m, py, J = 4.8, 1.6 Hz), 7.81 (1H, m, py, J = 7.2, 1.6 Hz), 7.94 (1H, dd, Pe, J = 6.8, 0.8 Hz), 8.40 (2H, s, phen), 8.64 (1H, s, py), 8.79 (1H, d, Pe, J = 8.4 Hz), 8.82 (1H, d, Pe, J = 8.4 Hz), 9.20 (2H, s, phen). ESI-MS: *m*/*z* observed 970.2991 (M$^+$), expected 970.3013.

An–xy–TMS 17. Synthesized in 60% yield from 9-bromoanthracene **16** and the asymmetric building block **8** using the general Suzuki coupling method. Purified by column chromatography on silica with pentane as an eluent. δ_H/ppm: 0.44 (9H, s, TMS), 1.54 (3H, s, Me), 2.48 (3H, s, Me), 7.04 (1H, s, xy), 7.34 (2H, ddd, An, J = 8.8, 6.4, 1.2 Hz), 7.46 (2H, ddd, An, J = 8.4, 6.4, 1.2 Hz), 7.47 (1H, s, xy), 7.54 (2H, dd, An, J = 8.8, 1.2 Hz), 8.05 (2H, d, An, J = 8.4 Hz), 8.48 (1H, s, An).

An–xy–I 18. Obtained from **17** using a TMS–halogen exchange procedure.[25] The yield was 90%. δ_H/ppm: 1.80 (3H, s, Me), 2.47 (3H, s, Me), 7.14 (1H, s, xy), 7.36 (2H, ddd, An, J = 8.4, 6.4, 1.2 Hz), 7.47 (2H, ddd, An, J = 8.8, 6.4, 1.2 Hz), 7.50 (2H, dd, An, J = 8.8, 1.2 Hz), 7.92 (1H, s, xy), 8.06 (2H, d, An, J = 8.4 Hz), 8.51 (1H, s, An).

An–xy–bpy 20. Synthesized by coupling **18** to bipyridine **19** with the general Stille coupling method. Purification occurred on a silica column using a 90 : 9 : 1 pentane–ethyl acetate–triethylamine eluent mixture. The yield was 25%. δ_H/ppm: 1.90 (3H, s, Me), 2.37 (3H, s, Me), 7.23 (1H, s, xy), 7.36 (1H, s, xy), 7.36 (1H, ddd, bpy, J = 7.6, 4.4, 1.2 Hz), 7.40 (2H, ddd, An, J = 8.4, 6.8, 1.2 Hz), 7.49 (2H, ddd, An, J = 8.8, 6.8, 1.2 Hz), 7.63 (2H, dd, An, J = 8.4, 0.8 Hz), 7.88 (1H, ddd, bpy, J = 8.4, 7.6, 1.6 Hz), 7.99 (1H, dd, bpy, J = 8.0, 2.4 Hz), 8.08 (2H, d, An, J = 8.8 Hz), 8.50 (1H, ddd, bpy, J = 8.4, 1.2, 0.8 Hz), 8.53 (1H, s, An), 8.54 (1H, dd, bpy, J = 8.0, 2.4 Hz), 8.75 (1H, ddd, bpy, J = 4.4, 1.6, 0.8 Hz), 8.86 (1H, dd, bpy, J = 2.4, 0.8 Hz).

[Re(An–xy–bpy)(CO)$_3$(py)]$^+$ 5. Obtained from the free ligand **20** and Re(CO)$_5$Cl following the general rhenium complexation method. The overall yield was 80%. $\delta_H$ppm: 1.93 (3H, s, Me), 2.38 (3H, s, Me), 7.30 (1H, s, xy), 7.39 (1H, s, xy), 7.4–7.5 (4H, m, An), 7.49 (1H, dd, bpy, $J = 6.4, 5.0$ Hz), 7.58 (2H, d, An, $J = 8.4$ Hz), 7.79 (1H, dd, bpy, $J = 8.0, 6.4$ Hz), 7.88 (1H, dd, bpy, $J = 8.0, 7.6$ Hz), 8.09 (2H, d, An, $J = 8.4$ Hz), 8.25 (1H, s, py), 8.26 (1H, d, py, $J = 4.4$ Hz), 8.36 (1H, dd, bpy, $J = 8.0, 7.6$ Hz), 8.48 (1H, d, bpy, $J = 8.0$ Hz), 8.54 (1H, s, An), 8.73 (1H, d, py, $J = 4.4$ Hz), 8.92 (1H, d, py, $J = 8.8$ Hz), 9.01 (1H, d, py, $J = 8.8$ Hz), 9.12 (1H, d, bpy, $J = 5.0$ Hz), 9.16 (1H, s, bpy). ESI-MS: m/z observed 786.1770 (M^+), expected 786.1761.

An–xy$_2$–TMS 21. Obtained following the general Suzuki coupling method with reactants **8** and **18**. Purified on a silica column using pure pentane as an eluent. The isolated yield was 50%. δ_H/ppm: 0.40 (9H, s, TMS), 1.83 (3H, s, Me), 2.11 (3H, s, Me), 2.23 (3H, s, Me), 2.51 (3H, s, Me), 7.12 (1H, s, xy), 7.14 (1H, s, xy), 7.18 (1H, s, xy), 7.37–7.41 (2H, m, An), 7.41 (1H, s, xy), 7.49 (2H, dd, An, $J = 7.6, 7.6$ Hz), 7.60 (1H, dd, An, $J = 8.4, 1.2$ Hz), 7.66 (1H, dd, An, $J = 8.4, 1.2$ Hz), 8.07 (2H, d, An, $J = 7.6$ Hz), 8.51 (1H, s, An).

An–xy$_2$–I 22. Obtained from **21** in essentially quantitative yield following a TMS–halogen exchange procedure.[25] δ_H/ppm: 1.84 (3H, s, Me), 2.18 (6H, s, Me), 2.48 (3H, s, Me), 7.14 (1H, s, xy), 7.15 (1H, s, xy), 7.20 (1H, s, xy), 7.39 (2H, ddd, An, $J = 8.8, 7.2, 0.8$ Hz), 7.48 (2H, ddd, An, $J = 8.0, 7.2, 0.8$ Hz), 7.58 (1H, dd, An, $J = 8.0, 0.8$ Hz), 7.63 (1H, dd, An, $J = 8.0, 0.8$ Hz), 7.81 (1H, s, xy), 8.07 (2H, d, An, $J = 8.8$ Hz), 8.51 (1 H, s, An).

An–xy$_2$–bpy 23. Synthesized from **19** and **22** following the general Stille coupling methodology. Purification was the same as for **20**. The yield was 20%. δ_H/ppm: 1.86 (3H, s, Me), 2.18 (3H, s, Me), 2.28 (3H, s, Me), 2.39 (3H, s, Me), 7.18 (1H, s, xy), 7.23 (1H, s, xy), 7.27 (1H, s, xy), 7.28 (1H, s, xy), 7.34 (1H, ddd, bpy, $J = 8.0, 4.8, 0.8$ Hz), 7.40 (2H, ddd, An, $J = 8.4, 7.6, 1.2$ Hz), 7.49 (2H, ddd, An, $J = 7.6, 5.6, 1.2$ Hz), 7.61 (1H, d, An, $J = 8.0$ Hz), 7.67 (1H, d, An, $J = 8.0$ Hz), 7.86 (1H, ddd, bpy, $J = 8.0, 7.6, 0.8$ Hz), 7.91 (1H, dd, bpy, $J = 8.0, 2.4$ Hz), 8.08 (2H, d, An, $J = 8.4$ Hz), 8.48 (1H, ddd, bpy, $J = 8.8, 1.2, 1.2$ Hz), 8.50 (1H, dd, bpy, $J = 8.0, 0.8$ Hz), 8.51 (1H, s, An), 8.73 (1H, ddd, bpy, $J = 4.8, 1.6, 0.8$ Hz), 8.79 (1H, dd, bpy, $J = 2.4, 0.8$ Hz).

[Re(An–xy$_2$–bpy)(CO)$_3$(py)]$^+$ 6. Obtained from the free ligand **23** and Re(CO)$_5$Cl following the general rhenium complexation method. The overall yield was 75%. δ_H/ppm: 1.86 (3H, s, Me), 2.17 (3H, s, Me), 2.33 (3H, s, Me), 2.42 (3H, s, Me), 7.19 (1H, s, xy), 7.20 (1H, s, xy), 7.30 (1H, s, xy), 7.36 (1H, s, xy), 7.38–7.47 (4H, m, An), 7.49 (1H, m, bpy), 7.60 (1H, d, An, 8.8), 7.65 (1H, d, An, 8.8), 7.78–7.92 (2H, m, bpy), 8.08 (2H, d, An, $J = 8.4$ Hz), 8.24 (1H, s, py), 8.25 (1H, d, py, $J = 4.8$ Hz), 8.34 (1H, dd, bpy, $J = 8.0, 7.6$ Hz), 8.39 (1H, d, bpy, $J = 8.4$ Hz), 8.52 (1H, s, An), 8.76 (1H, d py, $J = 4.8$ Hz), 8.86 (1H, d, py, $J = 8.4$ Hz), 8.94 (1H, d, py, $J = 8.4$ Hz), 9.11 (1H, s, bpy), 9.15 (1H, dd, bpy, $J = 4.8, 4.8$ Hz). ESI-MS: m/z observed 890.2411 (M^+), expected 890.2387.

Results and discussions

Synthesis

The target molecules (Scheme 1) were obtained following the synthetic strategy shown in Scheme 2. The commercially available 9-bromophenanthrene (**7**) and 9-bromoanthracene (**16**) molecules were coupled to the asymmetric *p*-xylene building block **8** (the synthesis of which has been described previously[21]) using a palladium(0) catalyzed (Suzuki) cross-coupling reaction. Trimethylsilyl–halogen exchange was effected with ICl, following a previously published protocol.[21] The resulting iodo-compounds **10** and **18** were then either subjected to reaction with another equivalent of the asymmetric *p*-xylene building block **8**, in order to lengthen the bridge, or they were coupled to pyridine **11**[22] and 2,2′-bipyridine **19**.[23] Pyridine Suzuki coupling occurred under identical conditions as the xylene couplings, *i.e.* in refluxing aqueous tetrahydrofuran solution in presence of a carbonate base and the Pd(Ph$_3$)$_4$ (Ph = phenyl) catalyst. 2,2′-Bipyridine Stille coupling required harsher conditions: **18**/**22** had to be reacted with **19** in refluxing *m*-xylene in the presence of the same catalyst for 5 d. Reaction yields were essentially quantitative for trimethyl–halogen exchange, between 25–95% for all Suzuki couplings, and only about 20% for the Stille couplings.

The organic ligands, **12** and **15**, were coordinated to rhenium by refluxing them with the [(Re(phen)(CO)$_3$Cl] and [Re(Me$_4$phen)(CO)$_3$Cl] precursors (phen = 1,10-phenanthroline, Me$_4$phen = 3,4,7,8-tetramethyl-1,10-phenanthroline) in 1,2-dichloroethane in the presence of a silver triflate.[10] Thereby, the complexes **1**, **2**, **3**, and **4** (Scheme 1) were obtained in variable yields. Ligands **20** and **23**, were first refluxed in toluene with commercial Re(CO)$_5$Cl. Then, the resulting Re(**20**)(CO)$_3$Cl and Re(**23**)(CO)$_3$Cl complexes were reacted with an excess of pyridine in toluene in the presence of a slight excess of silver triflate.[10,20] Thus, the target complexes **5** and **6** were obtained.

Optical spectroscopy

The solid lines in Fig. 1 are the optical absorption spectra of the mono-*p*-xylene dyads **1**, **3**, and **5** in dichloromethane solution.

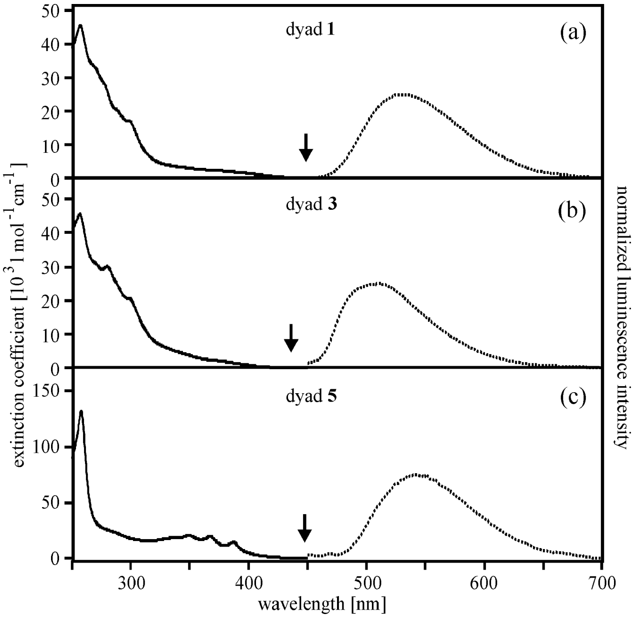
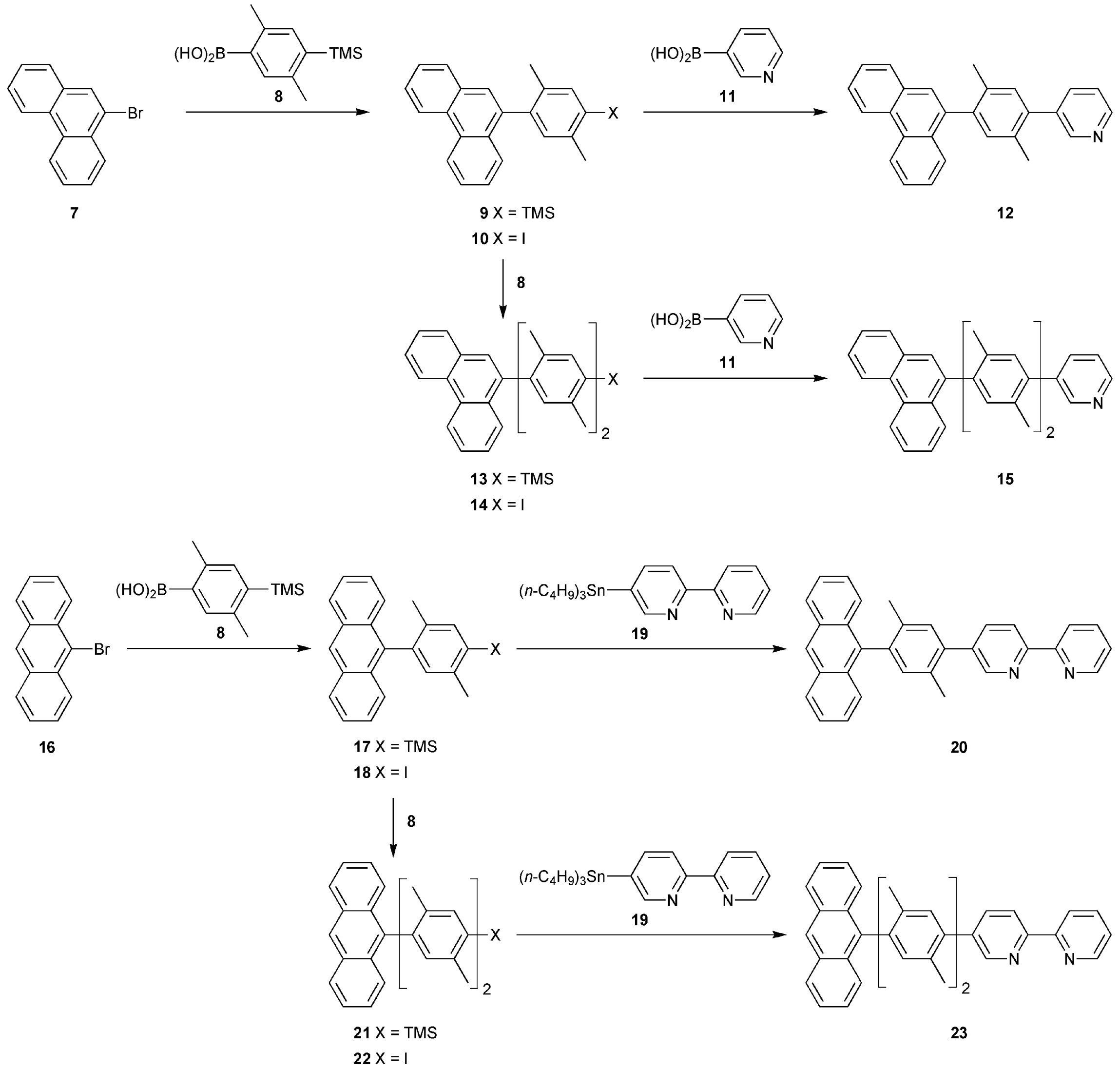


Fig. 1 Solid traces: optical absorption spectra of dyads **1** (a), **3** (b), and **5** (c) in dichloromethane solution. Dashed traces: luminescence spectra for the same compounds measured after 380 nm excitation in dichloromethane. Arrows mark the electronic origins of the emissive ^{3}MLCT state.



Scheme 2

The corresponding bi-*p*-xylene dyads **2**, **4**, and **6** have absorption spectra that are superimposable onto those shown in Fig. 1a, 1b, and 1c, respectively. This shows that xylene bridge lengthening does not alter the π-conjugation between the individual parts of the individual donor–bridge–acceptor molecules, in clear contrast to what is commonly observed for unsubstituted phenylene bridges. In oligo-*p*-phenylenes, there is a ~30° dihedral angle between individual phenyl planes,[24] whereas in oligo-*p*-xylenes that dihedral angle must be significantly greater for steric reasons. Indeed, recent work shows that molecular bridges, with up to five *p*-xylene units, have essentially length-independent HOMO–LUMO energy gaps.[25] Additional support for this comes from crystallographic studies, which found that in the solid state, the two phenyl rings of an unsubstituted biphenyl molecule can be almost co-planar,[26] whereas the two xylyl rings in a bi-*p*-xylene molecule were orthogonal to one another.[27]

Phenanthrene has no intense (>10^2 $M^{-1}cm^{-1}$) absorptions at wavelengths longer than 300 nm.[28] Consequently, the absorption spectra of **1** (Fig. 1a) and **3** (Fig. 1b) in the 300–450 nm spectral range are identical to $[Re(phen)(CO)_3(py)]^+$ and $[Re(Me_4phen)(CO)_3(py)]^+$ reference complexes that lack the phenanthrene unit.[10,12] Indeed, only some of the fine structure observed below 300 nm can be attributed to the phenanthrene, as the rhenium complex provides the dominant absorption features also between 250–300 nm; the extinction coefficients that are observed essentially correspond to those reported for the above mentioned reference complexes.[10,12] By contrast, the absorption spectrum of **5** (Fig. 1c) is dominated by anthracene bands rather than absorptions that are due to the rhenium complex: The intense (ε ~ 140 000 $M^{-1}cm^{-1}$) band around 260 nm as well as the weaker structured features observed between 340–390 nm are well-known anthracene absorptions.[29] The latter, commonly assigned to the S_0 ($^1A_{1g}$) → S_1 ($^1B_{1u}$) and S_0 ($^1A_{1g}$) → S_2 ($^1B_{1u}$) electronic transitions, overlap spectrally with the Re → bpy MLCT excitations. The bpy intra-ligand π–π* transitions are masked completely by the anthracene absorptions.

While in absorption striking similarities are observed between all four phenanthrene-based donor–bridge–acceptor molecules, steady-state luminescence experiments yield different results (dashed traces in Fig. 1). Notably, for the Me_4phen systems **3**

Table 1 Photophysical parameters for the six dyads

Dyad	E_{MLCT}/eV[a]	E_{T1}/eV	$\tau_X/\mu s$	$\tau_{ref}/\mu s$	k_{EnT}/s^{-1}
1	2.76	2.70[b]	2.57	2.88	$<3 \times 10^4$
2	2.76	2.70[b]	2.74	2.88	$<3 \times 10^4$
3	2.82	2.70[b]	7.0	13.0	6.6×10^4
4	2.82	2.70[b]	12.9	13.0	$<8 \times 10^3$
5	2.73	1.82[c]	0.015	0.63	7.0×10^7
6	2.73	1.82[c]	0.040	0.63	2.3×10^7

[a] From this work and ref. 10 and 12. [b] From ref. 31. [c] From ref. 29.

and **4**, the emission band maxima are blue-shifted relative to the phen systems **1** and **2** by about 800 cm^{-1}. This is due to the electron-donating nature of the methyl substitutents of the phenanthroline ligand. This raises the Re → phen MLCT energy and is an effect that has been observed previously for the $[Re(phen)(CO)_3X]^{n+}$ and $[Re(Me_4phen)(CO)_3X]^{n+}$ (X = Cl, pyridine; n = 0, 1) reference complexes.[10,12,30] The reference molecules with X = pyridine have emission spectra that are virtually identical to those shown in Fig. 1a and 1b, which confirms the hypothesis that electronic donor–bridge–acceptor coupling is weak in our molecules. Careful comparison of the absorption tails beyond 350 nm for dyads **1** and **3** and reveals that the MLCT blue-shift is also observed in absorption. The ^{3}MLCT energies (E_{MLCT}), estimated from these absorption and emission data, are given in Table 1. They are also marked by the arrows in Fig. 1.

The anthracene systems **5** and **6** have emission spectra (Fig. 1c) that are essentially identical to that observed for the $[Re(bpy)(CO)_3(py)]^+$ reference complex,[10] *i.e.* electronic donor–bridge–acceptor coupling is weak in these dyads, too. The emission band maximum as well as the E_{MLCT} are slightly red-shifted in the bpy systems **5** and **6** relative to the phen systems **1** and **2**. All E_{MLCT} values extracted from this analysis are summarized in the second column of Table 1.

While the luminescence *bandshapes* are identical within a homologous series comprised of a reference complex, the mono-*p*-xylene, and the bi-*p*-xylene bridged dyad, the luminescence *intensities* and *lifetimes* may still be expected to vary considerably between the individual members of such a series. However, this is only partly observed. Fig. 2a shows the luminescence decays of dyads **1** (solid trace) and **2** (dashed trace) in deoxygenated dichloromethane solution. Two virtually identical single exponential decays are observed. The MLCT lifetimes determined from these data are 2.57 (**1**) and 2.74 μs (**2**), which are identical, within 15% error, to the MLCT lifetime of the $[Re(phen)(CO)_3(py)]^+$ reference complex, which is 2.88 μs under identical experimental conditions. This indicates that the MLCT states in **1** and **2** are essentially unperturbed by the presence of the *p*-xylene bridges and the phenanthrene moiety. The emission properties of the three systems are in fact essentially indistinguishable from one another, and the conclusion is that in dyads **1** and **2**, rhenium-to-phenanthrene energy transfer is not competitive with other MLCT deactivation pathways.

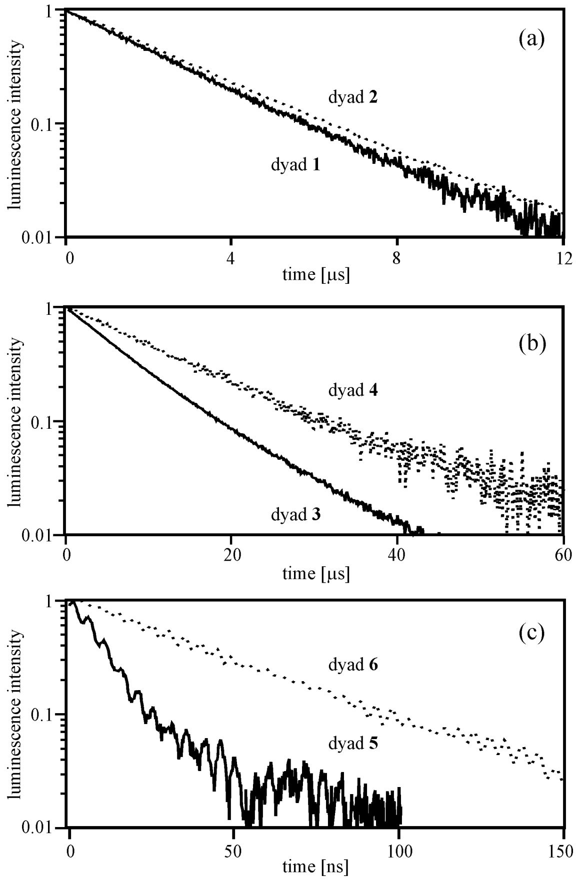


Fig. 2 MLCT luminescence decays of the six dyads in deoxygenated dichloromethane. Excitation occurred at 355 nm or 410 nm with 10 ns laser pulses, detection was at 560 nm. Note the three different timescales.

A different result is obtained for the Me$_4$phen systems **3** and **4**, see Fig. 2b. The decay trace of **4** is essentially identical to that of the reference complex $[Re(Me_4phen)(CO)_3(py)]^+$; the MLCT lifetime is 12.9 μs in deoxygenated dichloromethane solution (Table 1). As in **1** and **2**, in dyad **4** rhenium-to-phenanthrene energy transfer is found to be inefficient. However, the MLCT decay observed for dyad **3** is clearly faster; it is a bi-exponential decay with a major (90%) component that has a lifetime of 7.0 μs and a minor (10%) component with a lifetime of 20.1 μs. The latter is attributed to a luminescent impurity and is not considered further. The 7.0 μs component is attributed to dyad **3**; the MLCT population of this molecule is thus found to decay almost twice as fast as that of the $[Re(Me_4phen)(CO)_3(py)]^+$ reference complex. This additional excited state quenching is attributed to rhenium → phenanthrene energy transfer, and its rate constant k_{EnT} can be determined from the relation[7e,32]

$$k_{EnT} = \tau_X^{-1} - \tau_{ref}^{-1} \tag{1}$$

where τ_X is the excited-state lifetime of the donor–bridge–acceptor molecule X and τ_{ref} is the lifetime of the appropriate reference complex. Thus, one obtains $k_{EnT} = 6.6 \times 10^4$ s^{-1} for the mono-*p*-xylene bridged dyad **3** (Table 1) whereas for the bi-*p*-xylene bridged dyad **4**, k_{EnT} must be less than a tenth of τ_4^{-1}.

The excited states of the anthracene dyads **5** and **6** decay on a completely different timescale, see Fig. 2c. The luminescence lifetimes τ_5 and τ_6 are ~15 and 40 ns, respectively. For comparison, the $[Re(bpy)(CO)_3(py)]^+$ reference complex has an MLCT lifetime of 630 ns. Thus, luminescence quenching is very efficient for the anthracene dyads **5** and **6**. Based on eqn (1), one estimates $k_{EnT} = 7 \times 10^7$ s^{-1} for the mono-*p*-xylene dyad **5** and $k_{EnT} = 2.3 \times 10^7$ s^{-1} for the bi-*p*-xylene dyad **6**.

The interpretation of this excited state quenching, in terms of rhenium-to-anthracene (triplet–triplet) energy transfer, is corroborated by the transient absorption data shown in Fig. 3. The upper part of this figure shows the transient absorption spectrum measured within a 50 μs time window, 500 ns after excitation of dyad **6** at 355 nm. This is the typical absorption spectrum of the lowest energetic anthracene localized triplet excited state.[3a,c,6a,33] The lower part of Fig. 3 shows the temporal evolution of the transient absorption signal of dyad **6** at 425 nm. The negative signal at $t \approx 0$ is attributed to luminescence. Then, there is a rapid (<400 ns) rise, which reflects rhenium-to-anthracene energy transfer. The anthracene triplet population decays subsequently with a lifetime of 42 μs in deoxygenated dichloromethane solution, which is a typical value for organic triplets.[29a]

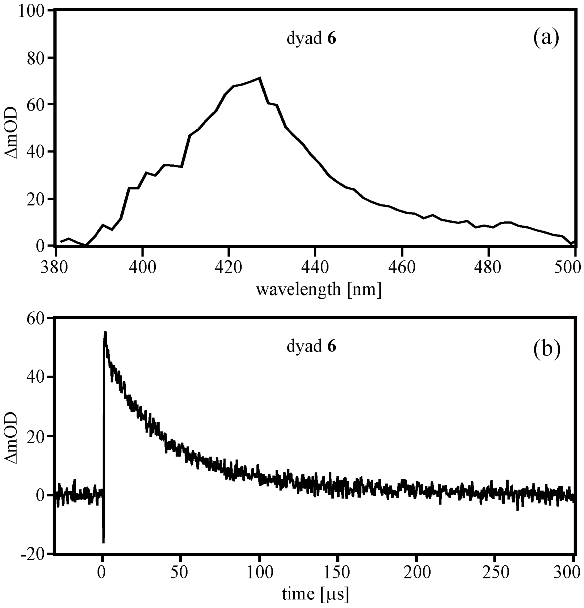
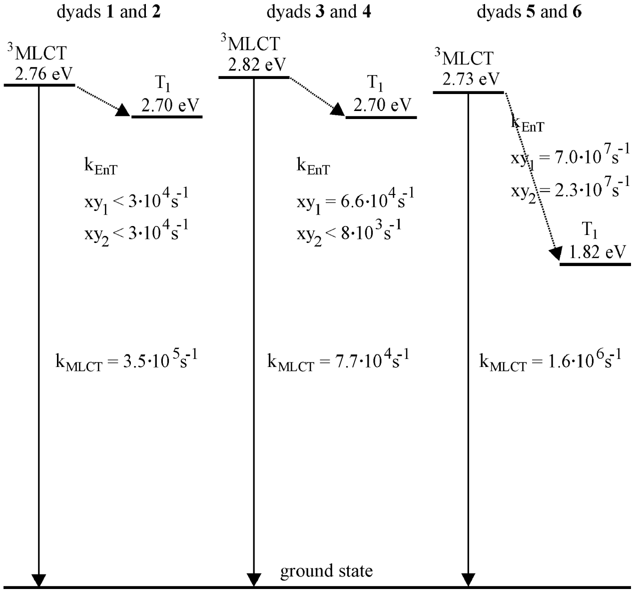


Fig. 3 (a) Transient absorption spectrum measured after 355 nm excitation of dyad **6** in deoxygenated dichloromethane solution. The spectrum was recorded in a 50 μs time window starting 500 ns after the excitation laser pulse at 355 nm. (b) Decay of the transient absorption signal from (a) at 425 nm.

Conclusions

The steady-state and time-resolved absorption and emission data presented in the prior sections allow us to establish the energy level diagram shown in Scheme 3. For dyads **1** and **2**, rhenium-to-phenanthrene energy transfer is not observed. This is due to the very low driving force ($-\Delta G^0 = 0.06$ eV) for this process. When the MLCT energy is raised relative to the phenanthrene triplet levels, triplet–triplet energy transfer becomes competitive with the inherent MLCT excited state deactivation ($-\Delta G^0 = 0.12$ eV), at least for dyad **3** with the short mono-*p*-xylene bridge. The bi-*p*-xylene spacer in dyad **4** is already too long for intramolecular energy transfer quenching to play a noticeable role. When the phenanthrene acceptor is replaced by anthracene, the energy transfer rate constants k_{EnT} increase by more than 3 orders of magnitude for both the mono-*p*-xylene and the bi-*p*-xylene bridged systems. The main reason for this observation must be the dramatic increase (~0.8 eV) in the driving force. It is possible, however, that the nature of the MLCT excitation also has some influence on k_{EnT}. In **5** and **6**, this excitation is localized right next to the xylene bridges and the anthracene acceptor, whereas in the other dyads, the MLCT excitation occurs on a molecular fragment that is separate from the xylene/phenanthrene moieties.



Scheme 3

Two important conclusions can be drawn from the bridge length variations performed in this study: (i) *p*-xylene bridge lengthening does not appear to influence the overall π-conjugation of the bridge (*i.e.* the bridge levels stay at constant energy) and, (ii) only the anthracene energy acceptor will be suitable for long-range energy transfer investigations with rhenium(I) tricarbonyl diimine donors.

An additional point is noteworthy: in dyad **6**, rhenium-to-anthracene energy transfer occurs through a bi-*p*-xylene unit over a distance of ~15 Å with a rate constant of 2.3×10^7 s^{-1} (Table 1). This is a rather low value considering that in an oligo-*p*-phenylene bridged Ru(II)–Os(II) dyad, energy transfer was found to proceed over 32.5 Å with essentially the same rate constant.[4] A recent study even reports on an energy transfer that occurs with a rate constant of 8.3×10^{11} s^{-1} through a biphenyl bridge.[34] There, energy transfer occurs *via* a hopping mechanism, which we can rule out for our system based on the relative inefficiency of the energy transfer process. However, even the super-exchange mediated energy transfer in the above mentioned Ru(II)–Os(II) dyad is orders of magnitude more efficient than in our rhenium–bixylene–anthracene molecule. A key difference between these two systems is the driving force for energy transfer. In our rhenium–anthracene dyads, this process is almost three times more exergonic than in the Ru(II)–Os(II) system. It is possible that inverted driving force effects play a role in our dyads.[35] Future investigations will shed more light on this issue.

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