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# Photoinduced Energy- and Electron-Transfer Processes within Dynamic Self-assembled Donor−Acceptor Arrays

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Received April 26, 2002

***Abstract:*** The synthesis and the photophysical properties of a series of noncovalently assembled donor−acceptor systems, dyads, is reported. The presented approach uses an “innocent” coordination compound, a scandium(III) acetyl acetonate derivative, as core and promotor of the dyad formation. Intercomponent photoinduced energy transfer or electron transfer within the dynamic assembly, which yields to a statistical library of donor−acceptor systems, is reported. The assemblies for energy-transfer processes are constituted by an energy donor, $\mathrm{Ru(bpy)_3}^{2+}$-based component (bpy = 2,2′-bipyridine), and by an energy-acceptor moiety, anthracene-based unit, both substituted with a chelating ligand, acetyl acetone, that via coordination with a scandium ion will ensure the formation of the dyad. If *N,N,N′N′*-tetramethyl-2,5-diaminobenzyl-substituted acetyl acetonate ligands are used in the place of 9-acyl-anthracene, intramolecular photoinduced electron transfer from the amino derivative (electron donor) to the $\mathrm{Ru(bpy)_3}^{2+}$-unit was detected upon self-assembly, mediated by the scandium complex. The photophysical processes can be studied on the lifetime of the kinetically labile complexes.

## Introduction:

Distance, relative orientation, and the molecular structure that separates a donor group from an acceptor moiety largely influence the feasibility of intramolecular electron- and energy-transfer processes.[1−4] To study the effect of these parameters, most of the effort has been devoted to the synthesis of covalently linked systems.[5−8] Self-assembly is a feature of modern chemistry,[9−13] which has been applied recently to arrange donor−acceptor dyads. In particular hydrogen bonding, salt bridges, and hydrophobic interactions have been investigated.[14−26] Surprisingly few examples that employ kinetically labile coordination compounds for assembly of the donor−acceptor units have been published.[27−32] The noncovalent approach offers some advantages: (i) the synthetic effort is reduced since only

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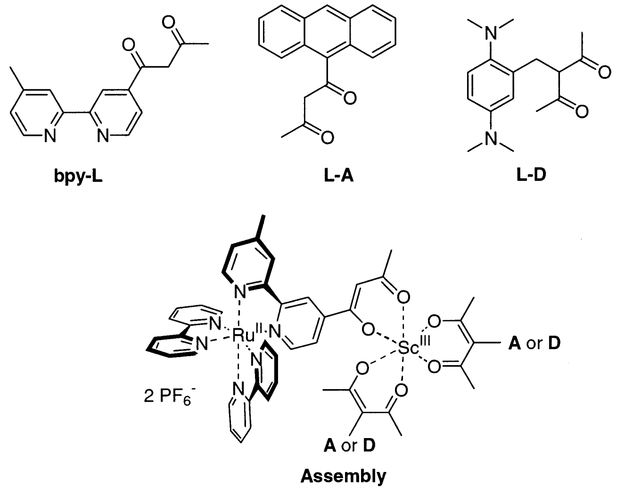
**10.1021/ja026695g CCC: $22.00**

***Scheme 1.*** Formulas of the Components **bpy-L**, **L-A**, and **L-D** and a Schematic Representation of Self-Assembled Dyads via the Coordination to the Scandium(III) Ion



substructures are prepared and self-assembled to obtain more complex architectures. The modular strategy allows the synthesis of different aggregates from only a few building blocks. (ii) The electronic interaction can be strongly modulated by solvent, temperature and concentration of the components. (iii) Electron- and energy-transfer processes can be studied over reversible bonds and longer distance, and new information is obtained on the electronic coupling via different linkages. However, several disadvantages must also be considered in this approach. The low association constants often prevent photophysical studies for which high-dilution conditions are required. Also in many cases (hydrogen bonds) the use of protic solvent is prevented.

We report here the synthesis and photophysical studies of a variety of photoactive components and their assembly. In particular the photoinduced processes in donor−acceptor dyads, obtained by the assembly of such components via an "innocent" metal ion, scandium(III), will be discussed. The high association constants, the possibility of success in many solvents, and finally the accessibility to many different components for the construction of our dyads are the most interesting features of our supramolecular structures. In these dynamic assemblies the scandium is only a structural motif that holds together an energy donor or electron acceptor, such as bis(2,2′-bipyridine)[4-{butane-1,3-dione-1-yl}-4′-methyl-2,2′-bipyridine]ruthenium(II)-bis(hexafluorophosphate), and an energy acceptor, 9-anthroylacetone, or an electron donor, 3-[2,5-(*N,N,N′,N′*-tetramethyldiamino)benzyl]-2,4-pentadione (see Scheme 1).

## Experimental Section

**Spectroscopy.** The UV−vis absorption spectra were recorded on a Hewlett-Packard diode array 84533 spectrophotometer. Recording of the emission spectra was done with a SPEX 1681 Fluorolog spectrofluorimeter. Lifetimes were determined using a Coherent Infinity Nd:YAG-XPO laser (1-ns pulses fwhm) and a Hamamatsu C5680-21 streak camera equipped with a Hamamatsu M5677 low-speed single-sweep unit. Transient absorption spectroscopy was performed by irradiation of the sample with a Coherent Infinity Nd:YAG-XPO laser (1-ns pulses fwhm). The sample was probed by a low-pressure, high-power EG&G FX-504 Xe lamp. The passed light was dispersed by an Acton SpectraPro-150s imaging spectrograph equipped with 150 or 600 g $mm^{-1}$ grating and tunable slit (1−500 $\mu$m) resulting in a 6- or 1.2-nm maximum resolution, respectively. The data were collected with a system containing a gaited intensified CCD detector (Princeton Instruments ICCD-576G/RB-EM) and an EG&G Princeton Applied Research model 9650 digital delay generator. $I$ and $I_0$ are measured simultaneously using a double 8 kernel 200 $\mu$m optical fiber with this OMA-4 setup. WINSPEC (V 1.6.1, Princeton Instruments), used under Windows, programmed and accessed the setup.

**Materials.** 4,4′-Dimethyl-2,2′-bipyridine (**1**),[33] 4′-methyl-2,2′-bipyridine-4-carboxylic acid (**2**),[34] 4′-methyl-2,2′-bipyridine-4-methylester (**3**),[35] rutheniumbisbipyridine dichloride,[36] 4-bromomethylene-4′-methyl-2,2′-bipyridine (**6**),[37] 2,5-(*N,N,N′,N′*-tetramethyldiamino)benzaldehyde (**10**),[38] and $Sc(acac)_3$[39,40] were synthesized according to established methods. All solvents employed for photophysical measurements were of spectroscopical grade and purchased from Aldrich. The benzonitrile used for the dynamic exchange of ligands was of HPLC grade and purchased from Aldrich.

**Synthesis. 4-(1,3-Butyldione)-4′-methyl-2,2′-bipyridine (4).** *N*-Isopropylidencyclohexylamine (247 mg, 1.7 mmol) was deprotonated in THF (20 mL) with 1.7 mmol LDA at 0 °C over a period of 30 min and slowly added to 365 mg (1.6 mmol) of **3**, stirred for 4 h at that temperature and additional 16 h at room temperature. After neutralization with 1 N HCl, the solution was diluted with $CH_2Cl_2$ and extracted several times with saturated aqueous $NH_4Cl$ and water. The organic layer was evaporated to dryness, and the crude product was purified by column chromatography (silica, $CH_2Cl_2/CH_3OH/NH_4OH$ 200:10:1) to yield 220 mg (54%). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.27 (s, 3H), 2.45 (s, 3H), 6.39 (s, 1H), 7.17 (m, 1H), 7.75 (m, 1H), 8.26 (s, 1H), 8.56 (m, 1H), 8.74 (s, 1H), 8.78 (m, 1H), 15.76 (b, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$, apt) $\delta$ 21.41 (−), 26.95 (−), 98.34 (−), 117.94 (−), 120.50 (−), 122.30 (−), 125.38 (−), 142.88 (+), 148.54 (+), 149.28 (−), 150.20 (−), 155.32 (+), 157.36 (+), 178.87 (+), 197.26 (+); IR (KBr) $\nu$ 2922, 1611, 1593, 1545, 1364, 1259, 1079, 831, 780, 841, 668, 514 $cm^{-1}$; MS (FAB) *m/z* 255.11 (100) [$M + H^+$], 154.01 (77); 136.03 (62)

**Bis(2,2′-bipyridine)-[4-(1,3-butyldione)-4′-methyl-2,2′-bipyridine]-ruthenium(II)-bis-(hexafluorophosphate) (5).** Bis(2,2′-bipyridine)-dichloro-ruthenium(II) dihydrate (390 mg, 0.75 mmol) was refluxed with 189 mg (0.74 mmol) 4-(1,3-butyldione)-4′-methyl-2,2′-bipyridine in 20 mL ethanol/water (3:1) for 4 h. The solvent was removed in vacuo and the residue dissolved in 10 mL of water. The remaining starting material was removed by multiple extraction with $CH_2Cl_2$ until the organic layer stayed clear. The crude product was precipitated as hexafluorophosphate from water to yield 520 mg (73%). $^1H$ NMR (300 MHz, $CD_3CN$) $\delta$ 2.31 (s), 2.59 (s), 6.67 (s), 7.32 (m) 7.39 (m), 7.44 (m), 7.59 (m), 7.75 (m), 7.89 (m) 8.09 (m), 8.55 (m), 8.80 (m), 15.76 (b); MS (ESI) *m/z* 813.13 (30) [$M^{2+}PF_6$], 334.08 (100) [$M^{2+}$]; $C_{35}H_{30}N_6O_2Ru$ calcd 668.147, found 668.16

**3-(4-Methylen-4′-methyl-2,2′-bipyridyl)-2,4-pentadione (7).** Sodium acetyl acetate (180 mg, 1.5 mmol) and 4-bromomethylen-4′-methyl-2,2′-bipyridine (**6**) (320 mg, 1.2 mmol) were refluxed in THF (30 mL) for 6 h. The reaction mixture was stirred overnight at room

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(39) $Sc(acac)_3$ was prepared by mixing $ScCl_3$ and an excess of 2,4-pentadione in dry methanol and deprotonation with ammonia gas, upon which the desired product precipitated out of the solution.

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temperature and evaporated to dryness. The residue was taken up in $CH_2Cl_2$ and washed with diluted acetic acid. Evaporation to dryness and chromatography ($SiO_2/CH_2Cl_2$-$CH_3OH$-$NH_3$ (25% in water), 100:5:0.5 (v/v), $R_f = 0.3$) yielded 180 mg (54%) of **7** as a yellow oil; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.09 (s, 6H pentadion-$CH_3$, enol-form), 2.18 (s, 6H pentadion-$CH_3$, keto-form), 2.44 (s, 6H, bipyridine-$CH_3$, keto- and enol-form), 3.22 (d, $3J = 7.4$ Hz, 2H, bipyridine-$CH_2$, keto-form), 3.75 (d, 2H, bipyridine-$CH_2$, enol-form), 4.13 (d, $3J = 7.4$ Hz, 1H, pentadion-CH, keto-form), 7.11 (m, 4H, bipyridine-H, keto- and enol-form), 8.24 (m, 4H, bipyridine-H, keto- and enol-form), 8.55 (m, 4H, bipyridine-H, keto- and enol-form), 16.89 (s, 1H, enol-OH); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 21.13 (+), 23.35 (+), 29.69 (+), 32.70 (−), 33.27 (−), 68.62 (+), 106.74 ($C_{quat}$), 120.49 (+), 120.97 (+), 121.98 (+), 122.03 (+), 122.28 (+), 124.06 (+), 124.80 (+), 124.84 (+), 148.16 ($C_{quat}$), 148.92 (+), 148.95 (+), 149.39 (+), 149.51 (+), 150.04 ($C_{quat}$), 155.61 ($C_{quat}$), 156.51 ($C_{quat}$), 192.01 ($C_{quat}$), 202.55 ($C_{quat}$); IR (film) $\nu$ 3054, 3007, 2923, 1727, 1595, 1428, 824 $cm^{-1}$; MS (70 eV, EI) $m/z$ 282 (22) [$M^+$], 267 (20) [$M^+ - CH_3$], 239 (100) [$M^+ - C(O)CH_3$], 43 (20) [$C(O)CH_3^+$].

**Bis(2,2′-bipyridine)[3-(4-Methylen-4′methyl-2,2′-bipyridyl)-2,4-pentadion]ruthenium(II)bis(hexafluorophosphate) (8).** Bis(2,2′-bipyridine)dichloro-ruthenium(II) dihydrate (310 mg, 0.6 mmol) and 3-(4-methylen-4′-methyl-2,2′-bipyridyl)-2,4-pentadione (180 mg, 0.64 mmol) were refluxed in ethanol/water (3:1, 20 mL). The dark red solution was evaporated to dryness, and the residue was purified by multiple gel permeation chromatography steps (Sephadex LH 20, $CH_3OH$), yielding 360 mg (73%) of **8** (chloride salt) as a dark red solid, mp 248 °C. Counterions were exchanged in water by treatment with aqueous $KPF_6$ to give **8** (PF6 salt) as an orange residue, mp 172 °C; TLC ($SiO_2$, $CH_3OH$−aqueous $NH_4Cl$−$CH_3NO_2$, 7:2:1, $R_f = 0.54$); $^1H$ NMR (400 MHz, $CD_3CN$) $\delta$ 2.10 (s), 2.13 (s), 2.51 (m), 2.89 (m), 3.00 (m), 7.22 (m), 7.37 (m), 7.52 (m), 7.69 (m), 8.03 (m), 8.34 (m), 8.46 (m); IR (KBr) $\nu$ 2958, 1605, 1483, 1466, 1427, 841, 556 cm-1; MS (ESI) $m/z$ 695 (28) [$M^+$], 261 (100).

**3-[2,5-(*N,N,N′,N′*-Tetramethylamino)benzylidene]-2,4-pentandione (11).** 2,5-(*N,N,N′,N′*-Tetramethylamino)benzaldehyde (**10**) (500 mg, 2.6 mmol) and 0.24 mL (2.4 mmol) of acetylacetone were combined with 2−3 drops of piperidine in 25 mL of dry chloroform and refluxed for 5 h. The mixture was evaporated to dryness. Column chromatography (silica, PE/EE 7:3) yielded 400 mg (61%) **11** ($R_f = 0.22$) of a dark-red oil. IR (KBr) $\nu = 2980$ $cm^{-1}$, 2941, 2865, 2829, 2789, 1686, 1658, 1505, 1242, 945; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta = 2.21$ (s, 3H, pentandione-$CH_3$), 2.41 (s, 3H, pentandione-$CH_3$), 2.65 (s, 6H, dimethylamino-$CH_3$), 2.83 (s, 6H, dimethylamino-$CH_3$), 6.61 (d, $4J = 2.9$ Hz, 1H, phenyl-H), 6.76 (dd, $3J = 8.8$ Hz, $4J = 2.9$ Hz, 1H, phenyl-H), 7.00 (d, $3J = 8.8$ Hz, 1H, phenyl-H), 7.87 (s, 1H, benzylidene-H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta = 26.73$ (+), 31.24 (+), 40.87 (+), 45.24 (+), 114.20 (+), 116.06 (+), 119.40 (+), 127.76 ($C_{quat}$), 139.74 ($C_{quat}$), 141.24 ($C_{quat}$), 144.34 ($C_{quat}$), 146.48 ($C_{quat}$), 197.17 ($C_{quat}$), 204.52 ($C_{quat}$); MS (70 eV), $m/z$ (%): 274 (100) [$M^+$], 231 (36) [$M^+ - CH_3CO$], 188 (22) [$M^+ - 2CH_3CO$].

**3-[2,5-(*N,N,N′,N′*-Tetramethylamino)benzyl]-2,4-pentandione (12).** A solution of 180 mg (0.65 mmol) of 3-[2,5-(*N,N,N′,N′*-tetramethylamino)benzylidene]-2,4-pentandione (**11**) and 10 mg of palladium/carbon (10%) in 50 mL of methanol was hydrogenated at $5 \times 10^6$ Pa hydrogen pressure for 1 h at room temperature. After filtration on Celite, the methanol was removed in vacuo, and the product was purified via column chromatography (silica, PE/EE 7:3). Yield: 140 mg (78%) **12** ($R_f = 0.44$) of a slightly yellow solid, mp 56 °C. IR (KBr) $\nu = 2978$ $cm^{-1}$, 2937, 2822, 2781, 1612, 1511, 1191, 947, 811; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta = 1.98$ (s, 6H, pentandione-$CH_3$, enol-form), 2.06 (s, 6H, pentandione-$CH_3$, keto-form), 2.50 (s, 6H, dimethylamino-$CH_3$, keto-form), 2.56 (s, 6H, dimethylamino-$CH_3$, enol-form), 2.77 (s, 6H, dimethylamino-$CH_3$, enol-form), 2.79 (s, 6H, dimethylamino-$CH_3$, keto-form), 3.09 (m, 2H, benzyl-$CH_2$, keto-form), 3.61 (s, 2H, benzyl-$CH_2$, enol-form) 4.07 (bs, 1H, pentandione-CH, keto-form), 6.34 (d, $3J = 3.0$ Hz, 1H, phenyl-H, enol-form), 6.41 (d, $3J = 3.0$ Hz, 1H, phenyl-H, keto-form), 6.53 (m, 2H, phenyl-H, keto- and enol-form), 6.99 (d, $3J = 2.7$ Hz, 1H, phenyl-H, keto-form), 7.01 (d, $3J = 2.7$ Hz, 1H, phenyl-H, enol-form); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta = 23.05$ (+), 27.74 (−), 29.39 (+), 30.91 (−), 40.88 (+), 40.98 (+), 45.37 (+), 45.59 (+), 68.88 (+), 109.18 ($C_{quat}$), 111.28 (+), 112.06 (+), 112.58 (+), 114.88 (+), 120.39 (+), 121.37 (+), 134.79 ($C_{quat}$), 135.52 ($C_{quat}$), 142.82 ($C_{quat}$), 147.60 ($C_{quat}$), 167.69 ($C_{quat}$), 191.85 ($C_{quat}$), 204.35 ($C_{quat}$); MS (70 eV), $m/z$ (%) 276 (100) [$M^+$], 233 (16) [$M^+ - CH_3CO$]. $C_{16}H_{24}N_2O_2$: calcd C 69.53 H 8.75 N 10.14; found C 69.46 H 8.82 N 10.10.

**General Method for the Assembly of Scandium Complexes.** Up to 10 mg of scandium-tris-acetylacetonate was dissolved with desired equivalents of ligands in 1 mL of benzonitrile. The solution was degassed, and a static vacuum of $10^{-3}$ Pa was applied. The reaction flask was left at room temperature while the solvent and all volatile compounds were collected in a liquid nitrogen-cooled flask. After complete evaporation of the solvent, the residue was redissolved and taken to dryness in the same manner twice, to ensure a complete exchange of ligands.

## Results and Discussion

**Design of a Dynamic Self-Assembled Donor−Acceptor Pair.** Acetyl acetonates (acac) are good ligands to complex trivalent metals ions, leading in the case of scandium(III) ions to thermodynamically stable (but kinetically labile) coordination compounds. The association constant in water for the formation of the hexacoordinated complex is $K_\beta > 10^{15}$ $M^{-1}$.[40] We can therefore expect that with such high $K_\beta$ complete association even at high dilution, necessary for photophysical investigations, occurs. The absorption spectra of Sc(III)$(acac)_3$ shows no bands at energy below 33500 $cm^{-1}$. This enables us to build up species containing energy- or electron donor and acceptor units that can be selectively excited in the visible region. Scandium(III) complexes cannot be oxidized, and with a redox potential of $Sc^{3+/2+}$ $E = -2.47$ V vs Fc/$Fc^+$, the complex will behave as an innocent spectator in electron-transfer processes between suitable donor and acceptor ligands coordinated to it.

Sc(III)$(acac)_3$ complexes are kinetically labile. The average lifetime of the complex is about 5 ms, before an acetylacetonate is exchanged.[41] Therefore, using a statistical approach such complexes can be dynamically assembled from a reservoir of available ligands. Depending on the choice of substituted acac ligands, an entire dynamic library of complexes can be created, from which some are able to constitute the correct building blocks for intramolecular energy- or electron-transfer processes. For our studies we have chosen two different substituents on the acac ligand, 3-[2,5-(*N,N,N′,N′*-tetramethyldiamino)benzyl]-2,4-pentadione as electron donor, **L-D**, and an acac ligand containing an anthracene unit, 9-anthroylacetone, **L-A,** as energy acceptor (see Scheme 1). The photosensitizer that behaves as electron acceptor or energy donor is a ruthenium complex, [Ru(**bpy-L**)$(bpy)_2$]$^{2+}$ (**bpy-L** = 1-(4′methyl-[2,2′bipyridinyl-4-yl)-butan-1,3-dione and bpy is 2,2′-bipyridine). The choice of these components is dictated by their well-known spectroscopic and electrochemical properties.

In particular the ruthenium complex has (i) an absorption in the visible where the other components do not absorb, allowing a selective excitation, (ii) the lowest excited state is luminescent,

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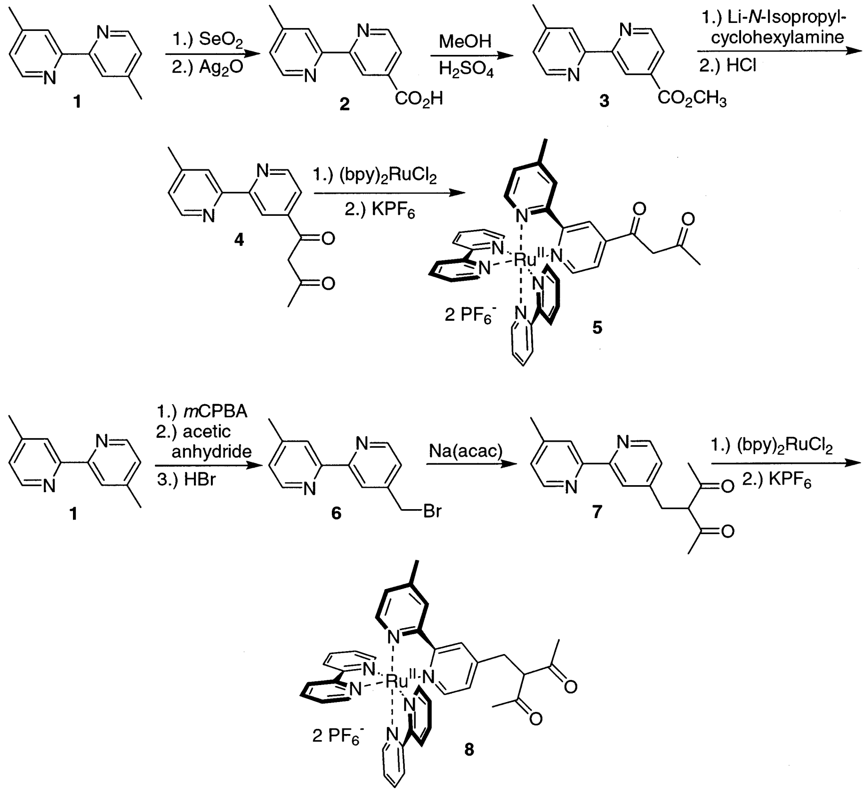
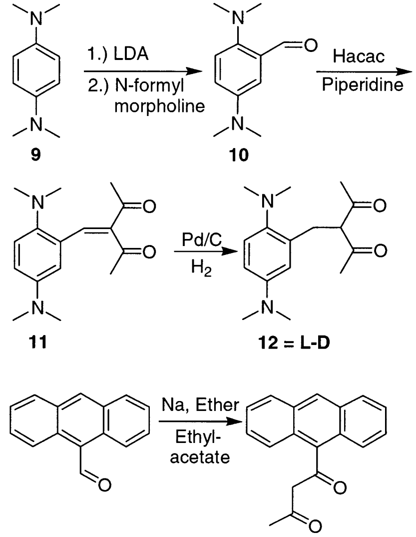
***Scheme 2.*** Synthesis of Ruthenium Tris-bipyridine Functionalized acac Ligands, Ru(bpy)$_2$(**bpy-L**)



and with lifetime of the order of hundreds of ns in acetonitrile.[42] This will allows us not only to observe even rather slow processes occurring in the excited states but also to treat the dynamic assemblies as discrete (static) molecular species in the excited state, therefore excluding chemistry in this time domain. Furthermore, because of the relatively easy substitution of the bipyridine ligands, it was possible to introduce the same type of chelating ligand, acac, on the Ru-based compound. We have therefore prepared and studied the Ru(bpy)$_2$(**bpy-L**)$^{2+}$ complex, **5**, that is able by self-assembly to coordinate a substituted scandium complex (containing the photoactive acac ligand, **L-D** or **L-A**) to form a suitable dyad for photoinduced energy transfer or electron transfer processes (see Scheme 1).

**Synthesis of the Photoactive Components.** Ruthenium tris-bipyridine complexes have been widely used to study photoinduced electron- and energy-transfer processes for their unique photophysical and redox properties.[42−44] The chemistry of bipyridines is very well explored and ensures the availability of suitable functionalized compounds.[45,46] The synthesis of a ruthenium complex with an acac binding site for scandium(III) ions is shown in Scheme 2. 4,4′-Dimethyl-2,2′-bipyridine (**1**)[33] was oxidized according to a two-step procedure, reported by McCafferty et al. with SeO$_2$ and Ag$_2$O.[34] The free carboxylic acid **2** was converted into the methyl ester **3**[35] and compound **bpy-L** (**4**) could be obtained upon addition of lithium-*N*-isopropyliden-cyclohexylamine and acidic workup in 54% yield.

***Scheme 3.*** Synthesis of Anthracene- and Tetramethyl Phenylenediamine-Functionalized acac Ligands



The ruthenium complex **5** was formed upon reaction of ruthenium-bis-2,2’-bipyridine dichloride with **bpy-L** in a mixture of water and ethanol. The product has been obtained as PF$_6$-salt in 73% yield.

To achieve a different connectivity between acac and bipyridine 4-bromomethylene-4′-methyl-2,2′-bipyridine (**6**)[37] was reacted with sodium acac to give **7** in 54% yield. Although the compound is a suitable ligand to give scandium acac complexes as confirmed by mass spectrometry, it could not be used to study photoinduced energy- and electron-transfer processes. Upon formation of the corresponding ruthenium complex **8** the ligand shows significant photolability with consequent decomposition.

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(42) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Zelewsky, A. v. *Coord. Chem. Rev.* **1988**, *84*, 85−277.

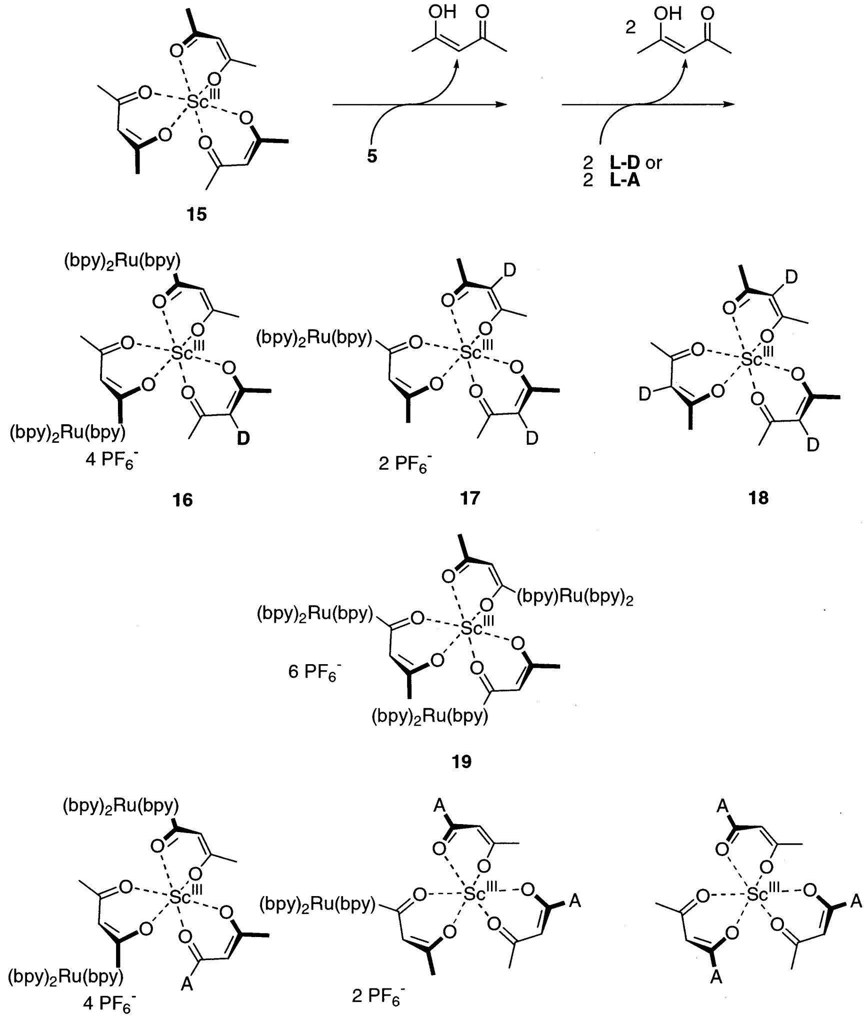
(43) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993−1019.

(44) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759−833.

(45) Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553−3590.

(46) Kröhnke, F. *Synthesis* **1976**, 1−24.

***Scheme 4.*** Preparation of Substituted Sc(III)(acac)$_3$ Complexes by Dynamic Ligand Exchange



For the synthesis of an acac ligand containing an electron donor group, **L-D**, commercially available tetramethyl-phenylendiamine was formylated[38] followed by a condensation reaction with acetyl acetone, to give the benzylideneacetylacetonate in 61% yield. Hydrogenation of the double bond led in 78% yield to the desired $\beta$-diketone **12** (**L-D**). The anthracene-acac conjugate **14** (**L-A**) was obtained following a procedure reported by Evans et al.[47] by reacting 9-acetylanthracene with ethyl acetate in the presence of sodium (Scheme 3).

**Formation of the Assemblies.** For the preparation of the dyads assembled via a scandium(III)(acac)$_3$ complex a mixture of the parent scandium(III) tris-acetylacetonate, **15**,[39,40] ruthenium complex **5**, and compound **L-D** or **L-A** were mixed in the appropriate stoichiometry in benzonitrile, and a pressure of $10^{-3}$ Pa was applied (see Scheme 4). Benzonitrile is a high-boiling solvent in which the PF$_6$-salt of the ruthenium complex is showing good solubility. Applying high vacuum to the mixture, the solvent and the unsubstituted acetylacetonate, the only volatile compounds, are slowly evaporated, driving the equilibrium toward the formation of the scandium complexes with substituted acac ligands. This procedure yields a statistical library of different scandium compounds, and assemblies **16**, **17**, **18**, and **19** are obtained when **L-A** is employed, while assemblies **19**, **20**, **21** and **22** are produced if **L-D** is one of the reagents, as shown in Scheme 4.

The ligand exchange can be monitored by NMR. The disappearance of the resonance of the characteristic proton at carbon 3 of 2,4-pentadione clearly indicates the exchange of unsubstituted acac ligands. A complete assignment of resonances is not possible due to the complexity of the mixture.

Assuming simple statistics with equal binding strength for all $\beta$-diketones the relative abundance of different substitution patterns can be calculated. All complexes were prepared in a stoichiometry of 1:2 of the ruthenium complex **5** to **L-D** or **L-A**, respectively. The theoretical relative abundance of the scandium complexes predict the least favorable complex bearing three ruthenium acac ligands (**19**) to be obtained in less than 4%. From this assembly only a luminescence contribution to the background of the emission spectra of the mixture is expected. Complexes bearing photoactive units and quenchers form the majority of all coordination complexes, 66%, and will give detectable indication of electron- or energy-transfer process. Assemblies not bearing any ruthenium complexes (**18** and **22**), present in 30%, will not contribute to absorption in the visible, where the excitation is going to be performed, or luminescence in the 550−800-nm region, where the ruthenium emission is monitored. Their absorption in the visible ($\lambda > 450$ nm) where

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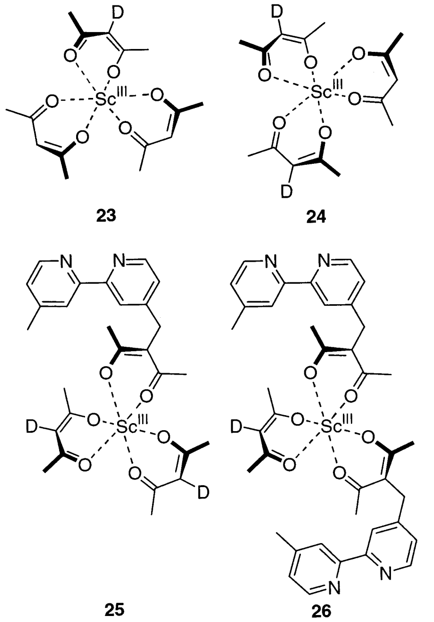
[47] Evans, D. F. *J. Chem. Soc* **1961**, 1987−1993.

***Scheme 5.*** Scandium(III) Complexes Detected by Mass Spectrometry



the ruthenium complex presents its metal-to-ligand charge-transfer (MLCT) bands is negligible. In the case of the anthracene-substituted acac ligands, the scandium complex **22** bearing three of these ligands is not soluble in benzonitrile and has been isolated from the mixture. Here we can assume to have a mixture of three different complexes in which at least one ruthenium-substituted acac ligand is present. Obviously no complete quenching of the luminescence of the ruthenium-acac compounds can be expected by formation of mixed scandium complexes. The abundance of complexes in the equilibrium having donor and acceptor ligand, such as **16/17** and **20/21**, is much less than 100%. In addition, a small amount of noncoordinated ruthenium ligands **5** may contribute to an unquenched background signal.

Mass spectrometry was used to monitor complex formation and distribution of ligands. In the EI mass spectra of the equilibrium mixture of Sc(acac)$_3$ (**15**) with 2 equiv of **12,** molecular ions of the complexes **15** ($m/z$ =342; 20%), **23** ($m/z$ = 518; 12%), **24** ($m/z$ = 694; 6%), and **18** ($m/z$ = 870; 4%), shown in Schemes 4 and 5, were detected.

This supports the assumption that all coordination compounds are present in the equilibrium. The different sensitivity of detection for each compound in EI-MS does not allow any quantitative conclusions. With ionization methods such as FAB or ESI, which allow a much better quantitative analysis, no scandium-containing complexes could be detected.[48]

Addition of 1 equiv of 3-(4-methylen-4′-methyl-2,2′-bipyridyl)-2,4-pentadione **7** to the mixture of complexes **15**, **18**, **23**, and **24** lead to detectable signals of the newly formed complexes **25** ($m/z$ = 876; 22%) and **26** ($m/z$ = 882; 8%) in the EI mass spectrum. This confirms the dynamic character of the mixture of coordination compounds. The given percentages for the molecules do not represent absolute abundance in solution. They only indicate the abundance of the detected fragments in the mass spectra.

More evidence for the formation of scandium complexes with mixed acac ligands and the dynamic character of the library will be provided in the photophysical section.

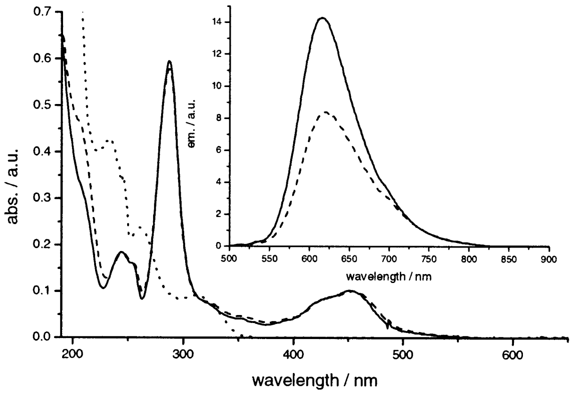


***Figure 1.*** UV−vis absorption spectra and room-temperature emission spectra (inset) of Ru(bpy)$_3^{2+}$ (full line), **5** (dashed line) $C \approx 10^{-5}$ M, and Sc(acac)$_3$ (dotted line) $C \approx 10^{-3}$ M in acetonitrile solutions.

***Table 1.*** Photophysical Data in Acetonitrile

| | Abs$_{max}$/nm | Em$_{max}$/nm | $\Phi_{aerated}$ | $\tau_{aerated}$/ns | $\tau_{deaerated}$/ns |
|---|---|---|---|---|---|
| **Ru(bpy)$_3$** | 455 | 614 | 0.016 | 160 | 890 |
| **5** | 458 | 624 | 0.011 | 150 | 525 |

**Photophysical Properties of 5 and Its Scandium Assembly.** The absorption and emission spectra of ruthenium complex **5** and of the reference compound Ru(bpy)$_3^{2+}$ in acetonitrile solution are reported in Figure 1. Some photophysical data are summarized in Table 1. The spectra show the characteristic $^1$MLCT bands in the visible region that in complex **5** are slightly red-shifted compared to the absorption of the parent compound. This can be explained considering that the lowest excited state involves the transition Ru → **bpy-L** since the acetylacetonate is a weak electron-withdrawing group. The direct substitution of the bpy with the acac moiety provides a good electronic coupling between the bpy and the acac group.[42] The UV region of the spectrum is dominated by the intense absorption bands of the bipyridine ligands (300 nm), and by comparison with the Sc(acac)$_3$ compound, the weak transition centered on the acac ligands (210 nm) can also be assigned. As already mentioned the scandium complex does not contribute to the absorption spectrum in the visible region.

The room-temperature emission spectrum in aerated acetonitrile solution (Figure 1, inset) shows a maximum at 624 nm also slightly red-shifted, compared with that of the reference complex, and in agreement with the assignment of a $^3$MLCT as the lowest excited state involving a transition from the Ru to the **L** ligand. The excited-state lifetime and the emission quantum yield are reported in Table 1.

Complexation of **5** to Sc(III) ions does not change the photophysical properties significantly.

**Self-Assembly of Energy Donor−Acceptor Dyads. Intramolecular Energy Transfer.** Upon appropriate choice of components it is possible to build up, using the scandium as "assembler", an energy donor−acceptor dyad. We have chosen an energy donor such as a ruthenium unit, **5**, and as energy acceptor an anthracene derivative, **L-A**. The two components have been previously investigated in covalently linked

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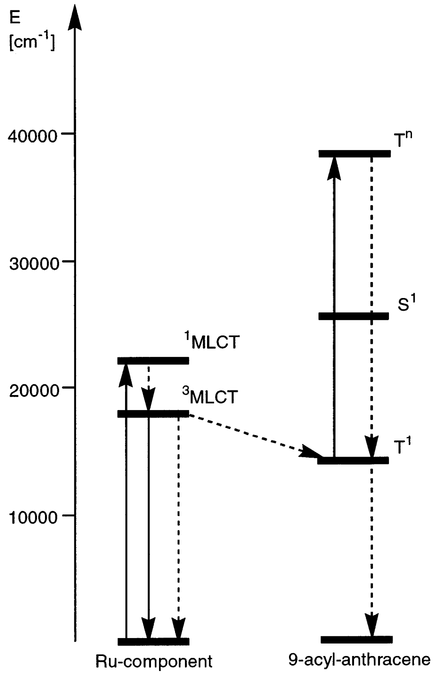
(48) Despite several attempts, we were not able to detect molecular ions of scandium complexes bearing one or more charged ruthenium-acac ligands using EI, ESI, FAB, MALDI mass spectrometry techniques.

***Scheme 6.*** Energy Diagram of Ru-Based Component and 9-Acyl-anthracene[a]



[a] Full arrows indicate radiative processes, whereas dashed arrows represent radiationless pathways.

systems,[49−51] and the energy-transfer processes from the excited ruthenium unit to the triplet excited state of the anthracene have been shown by emission quenching[50] and time-resolved spectroscopy.[49]

We expect on the basis of the energetics (see Scheme 6) a triplet−triplet energy transfer from the ruthenium moiety to the 9-acyl-anthracene, since we are exciting in the $^1$MLCT band of the transition metal complex. At such energy in fact, population of the singlet excited state of the anthracene moiety cannot occur.

In the assembly process a static distribution of species is possible, and an interesting library of compounds is obtained. The only assemblies that will give a photoinduced energy-transfer process are those containing both, one or two units of **5** and one or two units of **L-A** (complex **20** and **21**, Scheme 4). For our investigation they will behave identically, and no attempts were made to separate them. On the other hand the formation of the assemblies containing only anthracene or ruthenium complex or both, even though it will make the measurements more complicated, will not influence the final results, aiming to investigate the energy-transfer process and determine its rate.

The absorption spectra of the separate components and of the assemblies are shown in Figure 2. In the assembly the visible region is dominated by the already mentioned MLCT bands of the ruthenium units, and the close UV region by the characteristic absorption bands of the anthracene moiety that also shows an intense band at 253 nm. Since $Ru(bpy)_3^{2+}$ is a known sensitizer for singlet oxygen and anthracene is known to form endoperoxides with singlet oxygen,[52] all experiments were carried out in oxygen-free acetonitrile solutions.

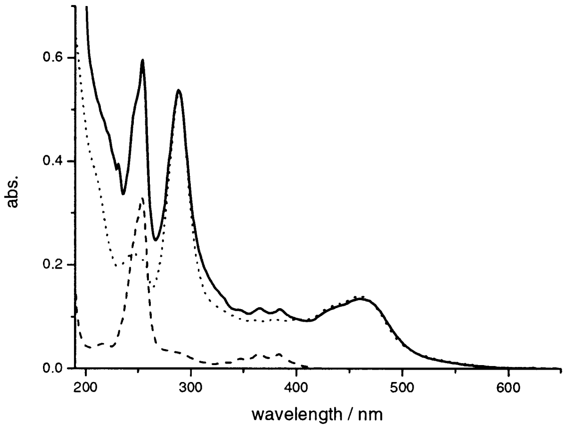


***Figure 2.*** UV−vis absorption spectra of **5** (dotted line), **LA** (dashed line), and the assembly of both (Ru−Sc-**L-A**) (full line) in deaerated acetonitrile solution. $C \approx 10^{-5}$ M.

As can be easily seen the spectrum of the adducts (containing one or two Ru-based moieties or one or two **L-A** units) is essentially the sum of the absorption spectra of **5** and **L-A**. This indicates that no strong ground-state electronic interaction between the two chromophores ($Ru(bpy)_3^{2+}$ and anthracene) is observed but does not indicate that the assembly is indeed formed when the components are mixed together. To have the proof of the formation of the assembly, steady-state and time-resolved spectroscopy has been employed.

The emission spectra of **5** and of the assembly show the characteristic luminescence of the Ru-based component but with different intensities. As one would expect, in the assembly a quenching of the emission is observed. This is in agreement with what was previously reported for covalently linked systems.[49−51] However an accurate evaluation of the luminescence quenching in the mixture is not possible only from the emission because of the statistical approach employed to build up the dyad. In fact the presence of free ruthenium complex, **5**, influences the total emission quantum yield, making the correct evaluation of the quenching impossible. It is interesting to notice, however, that the presence of free anthracene eventually does not corrupt our measurements since the fluorescence of the anthracene is located in a region (400−500 nm) that does not overlap with the ruthenium emission.

To have a quantitative evaluation of the quenching and to understand the process, responsible for the decrease in the emission intensity, time-resolved measurements were performed. The excited-state lifetime of compound **5**, measured under deaerated conditions, detected at about 620 nm, was 525 ns (see Table 1). A monoexponential model describes the observed decay trace. Within the assembly of **5** and **L-A** through the scandium complex (adduct **20** or **21**) the excited-state lifetime monitored at 650 nm, shows a biexponential behavior. The long-lived component has a lifetime identical to that of the unquenched complex **5**. The short component of the decay trace is calculated to have a lifetime of 4 ns.

The quenching process can be due in principle to two different mechanisms: photoinduced electron transfer from the anthracene to the ruthenium moiety or energy transfer from the excited

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(49) Boyde, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7448−7454.

(50) Belser, P.; Dux, R.; Baak, M.; De Cola, L.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 595−598.

(51) De Cola, L.; Balzani, V.; Belser, P.; Dux, R.; Baak, M. *Supramol. Chem.* **1995**, *5*, 297−299.

(52) Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH: Weinheim, 1995.

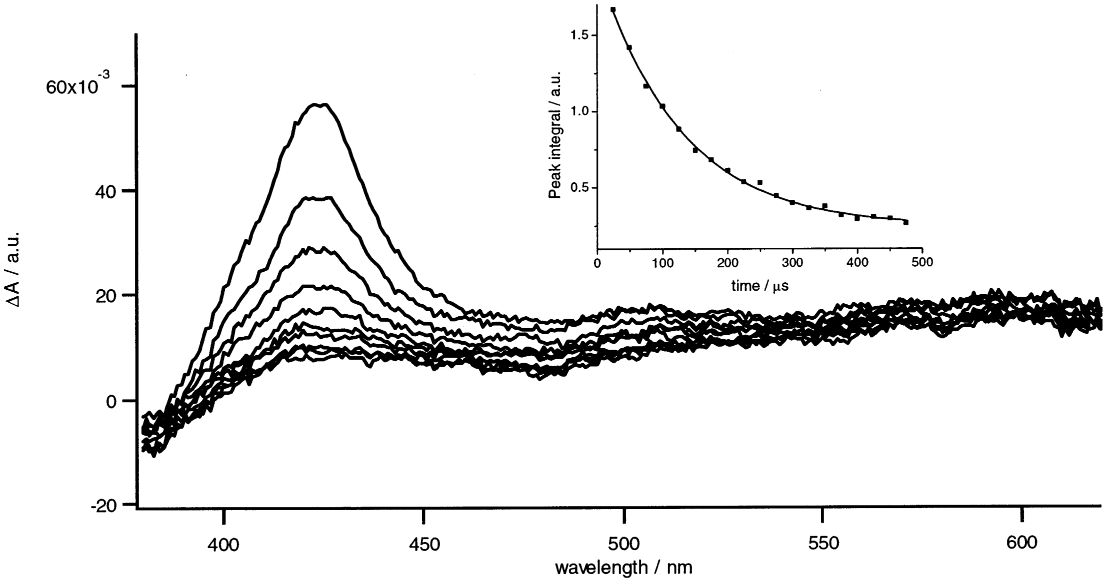

***Figure 3.*** Transient absorption spectra of the ruthenium−anthracene assembly in deaerated acetonitrile (time frame 50 $\mu$s). (Inset) Kinetics of the decay trace measured at 425 nm.

ruthenium unit to the lowest excited state of the anthracene. The electron-transfer process can be ruled out because of the endoergonicity of the process ($\Delta G = +0.32$ V).[53] The occurrence of energy transfer from the Ru-based to the anthracene-based component can be explained on the basis of the schematic energy level diagram (Scheme 6), showing that the energy is transferred from the $^3$CT Ru-based excited state to the lowest triplet excited state of anthracene ($T_1$), which then is radiationless deactivated to the ground state. The driving force for this exoergonic process is $\Delta G = -0.30$ eV, as calculated from the involved energy levels.[53]

In such a process the lowest triplet excited state of anthracene must be populated, and time-resolved transient spectroscopy has indeed shown that a strong absorption band is formed after the laser pulse (2 ns) at about 430 nm which has a lifetime of $\tau = 125$ $\mu$s (Figure 3). As already shown,[49] this band is characteristic of a triplet−triplet absorption, and the extremely long lifetime in deaerated solution confirms this assignment.

The efficiency of the energy transfer in the experimental conditions used ($C \approx 10^{-5}$ M) excludes any possible bimolecular process. However, to gain further proof that the Ru complex and the anthracene are linked via the Sc unit a photochemical experiment was performed. Upon irradiation in aerated solution with a 250-W Xe-lamp, equipped with an interference filter to select the 460-nm band of the $Ru(bpy)_3^{2+}$, the absorption spectrum of the assembly changes dramatically (Figure 4). In particular the disappearance of the anthracene bands at 250 and 340−400 nm is observed. On the other hand, the emission intensity of the Ru-based component increases up to 50% over the irradiated period.

The results obtained in aerated solution can be interpreted by sensitization via the Ru-based $^3$CT excited state of the Ru−Sc-anthracene (**Ru−Sc-An**) assembly, with formation of singlet oxygen (eq 1), followed by attack of singlet oxygen on an anthracene ring to form an endoperoxide derivative (eq 2), which then may evolve to give other products (indicated by **Ru−Sc-X**) where the central ring of anthracene has lost its aromatic character (eq 3):[52,54]

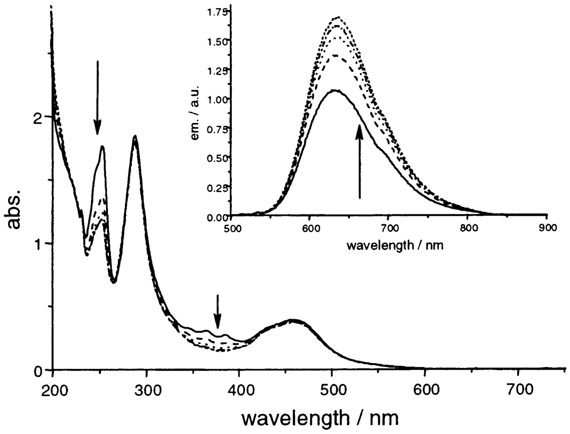

***Figure 4.*** Absorption spectra of the ruthenium−anthracene assembly ($C \approx 3 \times 10^{-5}$ M) at $t = 0$ (full line) and after 1, 2, 3, and 4 h (broken lines) of illumination in aerated acetonitrile. (Inset) Emission spectra under same conditions.

$$\textbf{Ru−Sc-An} + O_2 \rightarrow \textbf{Ru−Sc-An} + (^1\Delta)O_2 \qquad (1)$$

$$\textbf{Ru−Sc-An} + (^1\Delta)O_2 \rightarrow \textbf{Ru−Sc-An}(O_2) \qquad (2)$$

$$\textbf{Ru−Sc-An}(O_2) \rightarrow \textbf{Ru−Sc-X} \qquad (3)$$

The quenching process operated by the anthracene-based moiety in the photoproducts (eq 3) (where the anthracene aromaticity has been destroyed and, as a consequence, the $T^1$ level is no longer the lowest excited state, Scheme 6) cannot occur. This result indicates that the $T^1$ excited state of anthracene does indeed play a role in the energy-transfer process, quenching the Ru-based emission observed for **Ru−Sc-An** and more importantly that the two units are connected.

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(53) Calculated from the $E^{00}$ of the Ru-based component (17170 cm$^{-1}$) and the energy of the lowest triplet state of 9-acyl-anthracene (14700 cm$^{-1}$) (see: Murov, S.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993).

(54) Schmidt, R.; H.-D. Bauer *J. Photochem.* **1986**, *34*, 1−12.

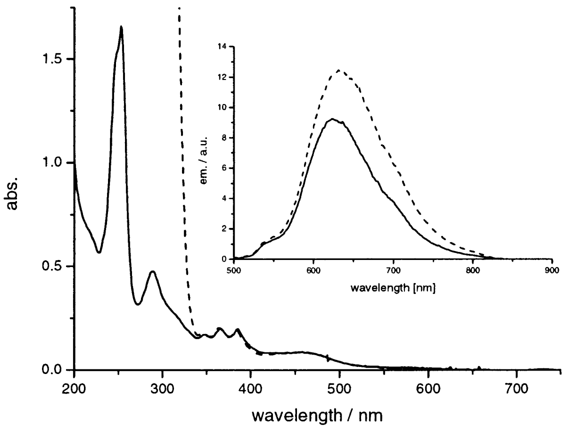


***Figure 5.*** Absorption spectra of **Ru−Sc-An** in acetonitrile (straight line) and upon addition of 2,4-pentadione (dashed line). (Inset) Emission spectra under same conditions. $C \approx 10^{-5}$ M.

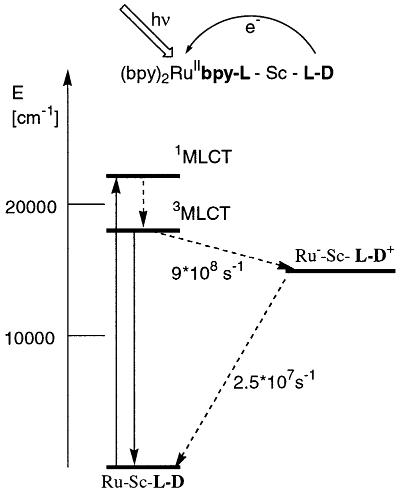
The same experiment has been performed at identical conditions, but using 1 equiv of **5** and 2 equiv of **L-A** without addition of any source of scandium ions. The absorption spectra show the same changes for the anthracene bands, over time, as those observed for the assembly. Obviously the ruthenium moiety still generates singlet oxygen upon irradiation, which reacts with anthracene to give endoperoxides in solution, effecting the absorption patterns of **L-A**. However, the ruthenium luminescence remained unchanged in this experiment because of no interaction with the anthracene.

Finally further evidence for the dynamic character of the assembly comes from a ligand competition study. An excess of 2,4-pentadione was added to a solution of the donor−acceptor assembly. Since the average lifetime of the scandium complexes is in the order of ms, a rather fast exchange of ligands was expected. The excess of 2,4-pentadione will lead to a disassembling of some of the dyad and the displacement of **L-A** with unsubstituted acetyl acetonate. The substitution of the 9-acyl-anthracene (quencher) with the “naked” acac would therefore lead to an increase in the emission intensity since the deactivation pathway (energy transfer) present in the assembly has been removed. Indeed the integration of the emission spectra before and after the addition of the 2,4-pentadione shows a significant increase of intensity up to 44% upon excitation in the isoabsorbative wavelength of 460 nm. The absorption spectra of the solution remains unchanged above 350 nm upon addition of excess of 2,4-pentadione (Figure 5).

From all these results we conclude that within the donor−acceptor scandium complexes **Ru−Sc-An** the emission of the Ru(bpy)$_3^{2+}$ moiety is quenched by a fast intramolecular triplet−triplet energy-transfer process from the Ru-based component to 9-acyl-anthracene-bearing ligands. The rate constant calculated from the quenched and unquenched ruthenium excited-state lifetime is $k_{en} = 2.5 \times 10^8$ s$^{-1}$.

**Self-Assembly of Electron Donor−Acceptor Dyads. Intramolecular Electron Transfer.** Substitution of the “naked” acac ligand with a 1,4-*N*,*N*,*N*′,*N*′-tetramethyldiaminobenzene derivative, **L-D**, leads to the possibility to build up an assembly containing an electron donor, **L-D** and an electron acceptor complex **5**. To have the same statistical complexes as in the previous section, **5** and **L-D** were mixed in a ratio of 1:2 in the presence of scandium ions.

***Scheme 7.*** Energy Diagram of the Assembly Ru−Sc-**L-D** with a Schematic Representation of the Photoinduced Electron-Transfer Process[a]



[a] Full arrows indicate radiative processes, whereas dashed arrows represent radiationless pathways.

To estimate any bimolecular electron-transfer contribution, **5** and **L-D** were mixed in a ratio of 1:2 in absence of scandium ions. The data showed no evidence for bimolecular processes under the experimental conditions ($C \approx 10^{-5}$ M, aerated acetonitrile) employed. In fact a monoexponential decay, ($\tau$ =150 ns) was observed that, as already discussed, corresponds to the value of the free ruthenium component **5** (see Table 1). In the presence of scandium ions under identical experimental conditions the formation of assemblies (**16**−**19**, see Scheme 4) can occur, and a dyad is formed. Such assembly formation can be followed spectroscopically since in **16** and **17** a decrease in the emission intensity of the Ru-based component should be expected on the basis of a thermodynamically allowed photoinduced electron transfer from the donor to the ruthenium component (Scheme 7). Indeed a quenching of the Ru-based component has been observed. The emission decay, monitored at 640 nm, becomes biexponential with a long component, due to the unquenched Ru(bpy)$_3^{2+}$ unit, and a short-lived component, $\tau = 10$ ns, due to the quenched luminescence. Upon light excitation an efficient electron transfer from the donor-based component, **L-D**, to the excited ruthenium unit (electron acceptor) is expected on thermodynamical grounds (Scheme 7). The process is in fact exoergonic ($\Delta G = -0.41$ V)[55] and in acetonitrile at room temperature is expected to be fast for the assembly. The rate calculated for the forward electron-transfer process is $k_{et} = 9 \times 10^8$ s$^{-1}$.

Oxidized tetramethyldiaminobenzene has a well-known absorption band between 500 and 750 nm. We have therefore used time-resolved transient absorption spectroscopy to detect the formation of the tetramethyl-phenylendiamino radical cation. Excited Ru(bpy)$_3^{2+}$ exhibits two absorption bands (bipyridinium radical anion), resulting from the transfer of an electron from the ruthenium to the bipyridine (MLCT transition), as can be clearly seen in Figure 6a. The absorption at 550 nm unfortunately overlaps with the band expected for the oxidized radical cation of **L-D**. Nevertheless, from a comparison between the

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(55) Calculated from the redox potentials of the single components, determined in 0.1 M TBAPF$_6$−CH$_3$CN against Fc/Fc$^+$ (**L-D**$^{0/+}$: −0.07 V.; Ru(bpy)$_3^{2+*/+}$: 0.34 V).

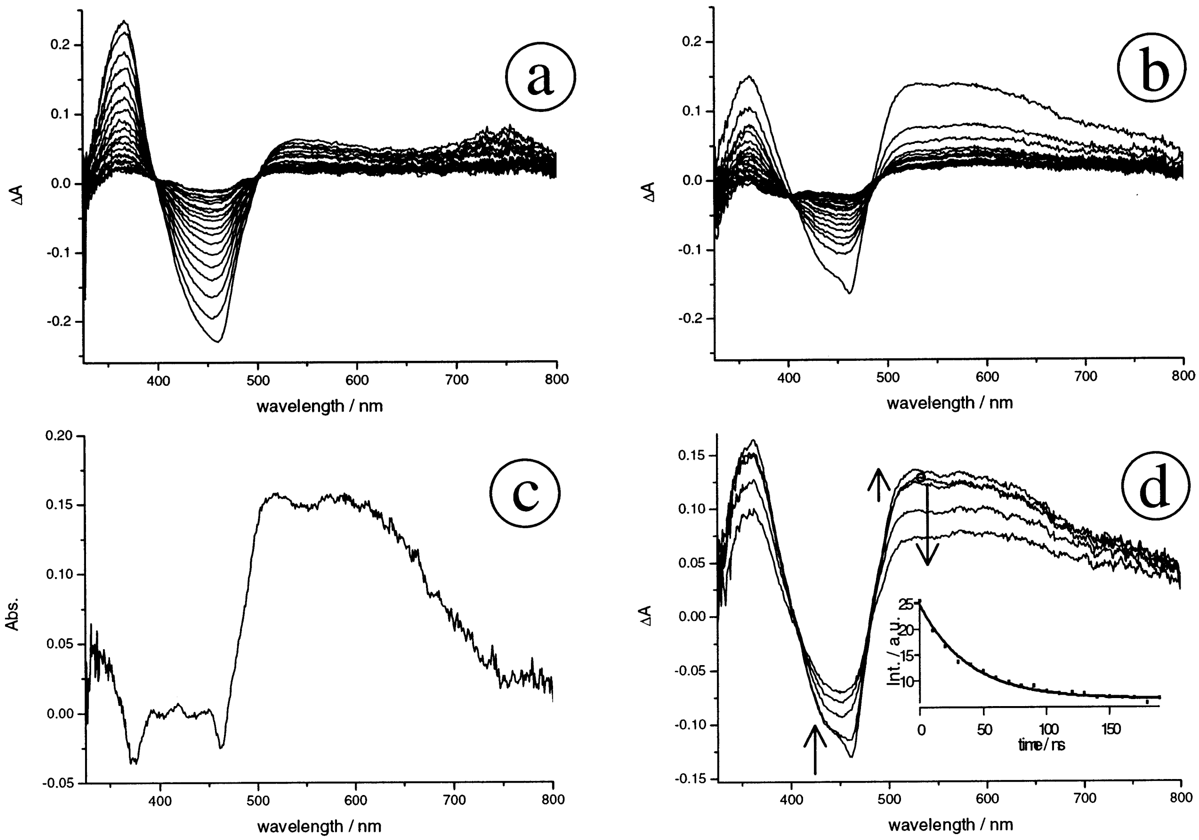

*Figure 6.* Transient absorption spectra of **5** (a) and $(bpy)_2Ru($**bpy-L**$)-Sc-$**L-D** (b), 25 ns time frame, excitation wavelength is 460 nm. (c) Difference spectra between (a) and normalized (b) frame 1. (d) Decay traces of $(bpy)_2Ru($**bpy-L**$)-Sc-$**L-D** after 1 (bold line), 2, 5, 10, and 20 ns. (Inset) Lifetime trace of the radical cation with $\tau = 40$ ns.

transient absorption spectra of **5** and those of the full assembly of **5** with Sc and **L-D** we are able to proof the formation of the characteristic radical cation of tetramethyl-phenylendiamine (Figure 6).

Figure 6a displays the spectra of **5**, recorded in acetonitrile with 25 ns between each frame with minimum instrumental gate time of 5 ns. The first frame was recorded at 1ns after the laser pulse. In the spectrum, the negative band at 460 nm is due to the bleaching of the ground state of $Ru(bpy)_3^{2+}$. The strong band at 375 nm and the weak band above 520 nm are due to the formed bipyridinium radical anion since a MLCT state is the lowest excited state. The ratio between these two bands is about 3:1. In Figure 6b we show the spectra of the full assembly $(bpy)_2Ru($**bpy-L**$)$-Sc-**L-D**, recorded under identical conditions. The band above 520 nm is much more dominant in this case, and the ratio between this one and the 375-nm band rose to almost 1:1. By normalizing the first frame of these two graphs to the same intensity of the bipyridinium radical anion band at 375 nm and subtracting them from each other, we obtained the transient absorption spectrum, displayed in Figure 6c.[56] By comparison with the spectra reported in the literature for the radical cation of tetramethyl-phenylendiamine,[56] it is clear that the transient in Figure 6c is indeed the same species. To follow the formation of the transient band at 550 nm (forward electron transfer) and its decay, that from the emission lifetime should occur within 10 ns, we performed the same transient spectra in shorter time scale (Figure 6d). As can be seen, the first spectrum does not correspond to the full formation of the radical cation, since the band is still growing after 2 ns. At longer delays (10, 20 ns) the decay of this species can be monitored, and a lifetime of $\tau = 40$ ns was estimated (see inset, Figure 6d). From the decay of the radical cation absorption, we have calculated the rate for the back-electron-transfer reaction, $k_{back} = 2.5 \times 10^7$ $s^{-1}$.

## Conclusions

Substituted $\beta$-diketones bearing either $Ru(bpy)_3^{2+}$ as an energy-donor or electron-acceptor component, 9-acyl-anthracene as acceptor moiety for energy transfer, or 1,4-*N*,*N*,*N*′,*N*′-tetramethyldiaminobenzene as electron-donating group have been used to form photoactive dyads around a Sc(III) ion by self- assembling. Assemblies obtained by coordination with Sc(III) ion having $Ru(bpy)_3$-based components and anthracene-substituted ligands show efficient intramolecular energy transfer from the excited ruthenium complex to the lowest excited state of the anthracene-bound component. Within scandium complexes of $Ru(bpy)_3$ and 1,4-*N*,*N*,*N*′,*N*′-tetramethyldiaminobenzene-substituted ligands photoinduced electron-transfer processes were detected. It is interesting to notice that even though the energy and electron donor−acceptor systems are not directly linked, the photoinduced processes are rather fast. The Sc(III) ion plays only a structural role and is not directly involved in the process. The use of the dynamic assembly strategy for the generation of photoactive donor−acceptor dyads provides access to systems which are not static and react on external stimuli.

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(56) A reference spectrum for the tetramethyl-phenylendiamino radical cation can be found, for example, at: Steenken, S.; Vieira, A. J. S. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 571−573.

Such systems are of high complexity, and their study is a challenge. However, due to their dynamic nature they may offer advantages for practical applications.

**Acknowledgment.** This work was supported by the Volkswagen Foundation. M.K. thanks the Graduate College Sensory photoreceptors, University of Regensburg, Germany, for support. H.Z. thanks the state of Niedersachsen for a graduate fellowship. We thank Dr. R. M. Williams for helpful discussion and his help in the preparation of the manuscript. We are grateful to the MS Service of the University of Fribourg/ Switzerland for high resolution ESI mass spectra.

JA026695G