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LETTERS

Closely-spaced chelating centers: synthesis of novel spiro-bridged bis-phenanthrolines and bis-indole derivatives

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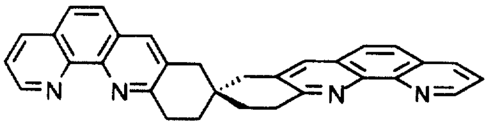
Abstract

The syntheses of novel soluble ditopic 1,10-phenanthroline ligands bearing a central spiro-[5.5]undecane or a spiro-[5.5]bifluorylidene fragment are reported. The synthetic approach is based on a Friedländer condensation between 8-amino-7-quinolinecarbaldehyde and either 3,9-diketospiro-[5.5]undecane or 2,2′-diacetyl-spiro[5.5]bifluorylidene derivatives. Reaction of the latter with phenylhydrazine and subsequent cyclization afforded 2,2′-di-(2″-indolyl)-[5.5]spirobifluorylidene. The photophysical properties of the new compounds are briefly discussed and Ru(II) and Cu(I) complexes were prepared. © 1999 Elsevier Science Ltd. All rights reserved.

Cascade energy transfer processes occurring in molecular arrays have attracted much attention aimed at mimicking the reactive center in natural photosynthesis.[1] Triplet–triplet energy transfer, often invoked as protective measures in photosynthetic organisms,[2] is also a convenient tool for transferring stored information at the molecular level.[3] A plethora of molecular scaffoldings have been studied in recent years,[4,5] especially those involving transition metal polypyridine complexes as the donor and acceptor subunits. A major drawback of many of these systems is that the respective donor and acceptor subunits are tethered by flexible bridges and diffusion processes cannot be properly separated from energy transfer processes.[6]



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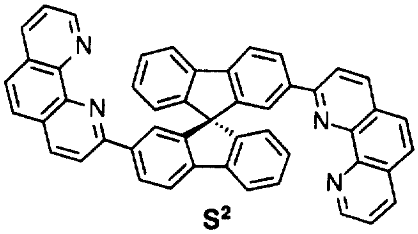

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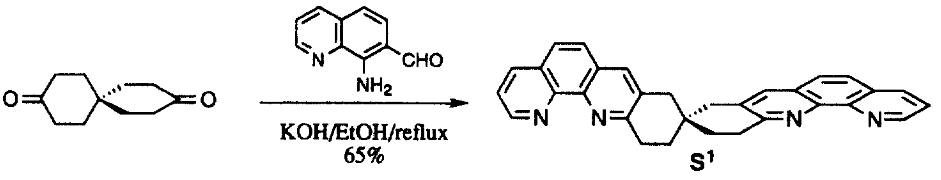
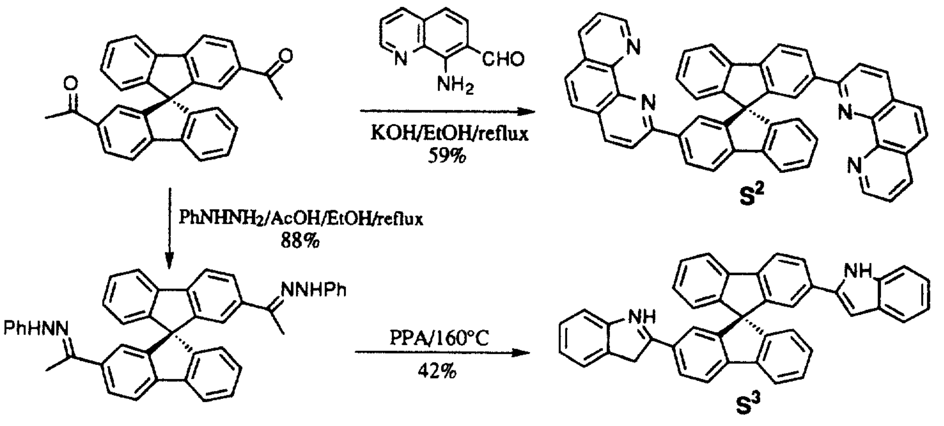
Continuing our investigations on energy-transfer processes in supramolecular assemblies involving luminophoric complexes, we have designed and prepared several rigid and closely-spaced spiro-bis-phenanthroline ligands using Friedländer methodology.[7] Because of their exceptional coordination properties, chemical stability and synthetic versatility, we chose the phenanthroline subunit as the key building block by which to construct the donor/acceptor dyads. The edge-to-edge distance between the two chelating fragments vary from ca. 7.6 to 4.5 Å in the fluorenyl case.

The spiro-[5.5]undecane derivative **S**^{1} is prepared by condensation of 3,9-diketospiro-[5.5]undecane[8] with 8-amino-7-quinolinecarbaldehyde[7] under basic conditions as outlined in Scheme 1. On the basis of spectroscopic evidence, the structure of **S**^{1} was unequivocally assigned.[9] Similarly, 2,2′-diacetyl-[5.5]spirobifluorylidene[10] was allowed to react with 8-amino-7-quinolinecarbaldehyde under Friedländer conditions to afford the spirobifluorylidene compound **S**^{2} (Scheme 2).[11]



Scheme 1.



Scheme 2.

Condensation of 2,2′-diacetyl-[5.5]spirobifluorylidene with phenylhydrazine in the presence of a trace amount of AcOH yielded the bisphenylhydrazone which, after heating with polyphosphoric acid (PPA), afforded the bis-indole derivative **S**^{3}.[12]

Spectroscopic and photophysical data for the three new ditopic species are summarized in Table 1. All of the ligands exhibit fluorescence bands in fluid solution at room temperature, and both fluorescence and phosphorescence in a rigid matrix at 77 K.

It is noteworthy that **S**^{2} and **S**^{3} feature a high luminescence quantum yield, presumably due to the presence of the fluorene subunit, which is known as a strong emitter (Φ=0.80).[13] By contrast, in **S**^{1} the fluorene subunit is no longer present, and the emission quantum yield is much lower.

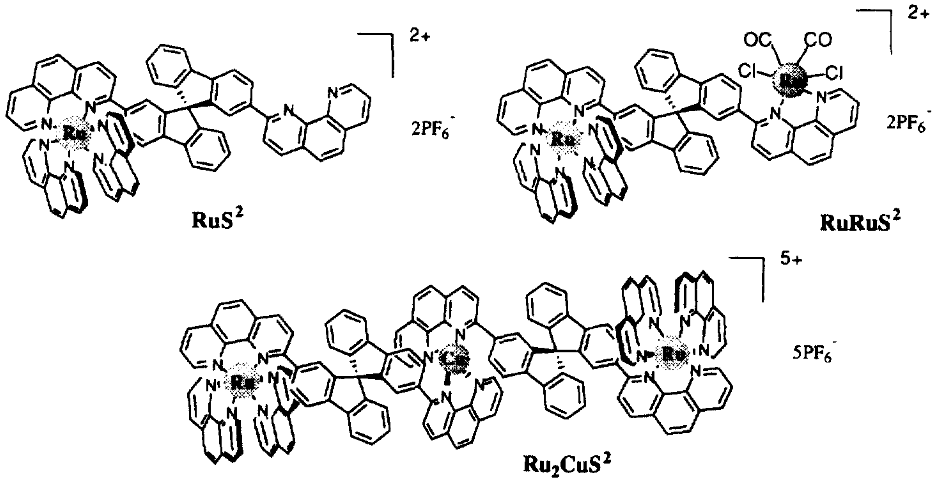
The spiro-based ligand **S**^{2} was used for the synthesis of several homo- and heteronuclear complexes. Indeed, coordination of one phen subunit could be achieved using $[Ru(phen)_2Cl_2]$[14] as the metal precursor. **RuS**^{1} was isolated in 95% yield and exhibited a characteristic MLCT absorption at 446 nm (ε=14 500 M^{-1} cm^{-1}). The FAB-MS exhibited a molecular peak at 1279.2 (corresponding to $[M{-}PF_6]$) and at 1134.1 (corresponding to $[M{-}2PF_6]$). Reaction of **RuS**^{2} with $[Ru(CO)_2Cl_2]_n$[15] in

Table 1
Selected spectroscopic and photophysical data for spiro ligands[a)]

Cmpd	Absorption λ_{max}, nm (ε, $M^{-1}cm^{-1}$) at 298 K	Luminescence				
		298 K			77 K	
		λ_{max}, nm	τ, ns	Φ_{em}	λ_{max}, nm	τ, μs
S^1	343 (1,980), 271 (64,600)	349	1.2	1.3×10^{-2}	348 $460^{b)}$	0.0053 1850,000
S^2	361 (24,400), 331 (36,700)	385	1.2	0.48	385 $518^{b)}$	0.0019 814,000
S^3	343 (65,200)	404	1.8	0.75	380 $539^{b)}$	0.0018 624,000

a) In acetonitrile solution at room temperature and in 4:1 (v/v) methanol/ethanol rigid matrix at 77 K.
b) Phosphorescence band.

methanol afforded a 29% yield of the dinuclear complex *trans*-(Cl)-[**RuRuS^2**] which displayed an FT-IR ν_{CO} at 2053 and 1961 cm^{-1}, FAB-MS molecular peak at 1506.9 (corresponding to [M–PF$_6$]), and a UV–vis band at 446 nm (ε=22 300 M^{-1} cm^{-1}). Finally, **RuS^2** was allowed to react under argon with [Cu(CH$_3$CN)$_4$]PF$_6$[16] and, after recrystallization, gave a 57% yield of the trinuclear **Ru$_2$CuS^2** complex which exhibited a molecular peak at 2912.2 [M–PF$_6$] and fragmentation peaks at 2767.2 [M–2PF$_6$] and 2622.2 [M–3PF$_6$] in the FAB-MS spectrum; as well as a UV–vis band at 447 nm (ε=32 300 M^{-1} cm^{-1}). The structures of these complexes are illustrated in Scheme 3.



Scheme 3.

In conclusion, we have synthesized novel, rigid and closely-spaced ditopic ligands by sequential condensation steps. These molecules make ideal building blocks for the preparation of luminescent transition metal complexes which have sufficient simplicity and versatility to provide the basis for a systematic study of triplet energy transfer in donor/acceptor dyads. Studies of their photophysical and electrochemical properties are currently under investigation and will afford an opportunity to examine the role of the spiro-phen spacer in such systems.

Acknowledgements

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9. ^{1}H NMR ($CDCl_3$) for [3,2-*b*; 9,8-*b*]-di-(1′,10′-phenanthrolino)-spiro[5,5]undecane $\mathbf{S^1}$: δ 9.18 (dd, 2H, *J*=4.2 Hz, 1.2 Hz, H_9), 8.21 (dd, 2H, *J*=8.1 Hz, 1.5 Hz, H_7), 7.82 (s, 2H, H_4), 7.66 (s, 4H, H_6 and H_5), 7.59 (dd, 2H, *J*=8.1 Hz, 4.5 Hz, H_8), 3.52 (m, 4H, $H_{4'}$ and $H_{8'}$), 2.97 (s, 4H, $H_{1'}$ and $H_{11'}$), 2.02 (m, 4H, $H_{5'}$ and $H_{7'}$); ^{13}C NMR ($CDCl_3$) δ 158.5, 150.0, 145.7, 144.2, 136.3, 136.0, 130.9, 128.3, 127.2, 126.1, 125.4, 122.5, 39.4, 33.2, 31.5, 29.9. mp 190°C (decomp). Anal. calcd for $C_{31}H_{24}N_4$: C, 82.30; H, 5.31; N, 12.39. Found: C, 82.61; H, 5.75; N, 12.53.
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11. ^{1}H NMR ($CDCl_3$) for 2,2′-di-(2″-[1″,10″]phenanthrolinyl)-[5.5]spirobifluorylidene $\mathbf{S^2}$: δ 9.14 (d, 2H, *J*=3.7 Hz, $H_{9'}$), 8.61 (d, 2H, *J*=7.9 Hz, $H_{4'}$), 8.16 (d, 2H, *J*=7.9 Hz, $H_{7'}$), 8.09 (d, 2H, *J*=4.7 Hz, $H_{3'}$), 8.06 (d, 2H, *J*=4.2 Hz, H_4), 7.94 (d, 2H, *J*=7.5 Hz, H_5), 7.81 (d, 2H, *J*=8.3 Hz, H_3), 7.66 (broad s, 2H, $H_{5'}/H_{6'}$), 7.56 (AB quartet, 2H, *J*=4.5 Hz, $H_{8'}$), 7.48 (s, 2H, H_1), 7.38 (t, 2H, *J*=7.5 Hz, H_6), 7.12 (t, 2H, *J*=7.4 Hz, H_7), 6.77 (d, 2H, *J*=7.5 Hz, H_8); ^{13}C NMR δ 157.6, 150.2, 149.5, 148.8, 146.3, 145.9, 143.2, 141.3, 139.8, 136.5, 136.0, 128.9(2C), 128.2, 127.8, 127.4, 126.3, 126.0, 124.2, 123.3, 122.7, 121.1, 120.7, 120.5, 66.8. mp >300°C. Anal. calcd for $C_{28}H_{18}N_2 \cdot 3H_2O$: C, 80.99; H, 4.68; N, 7.71. Found: C, 81.16; H, 4.66; N, 7.50.
12. ^{1}H NMR (DMSO-d_6) for 2,2′-di-(2″-indolyl)-[5.5]spirobifluorylidene $\mathbf{S^3}$: δ 11.35 (s, 2H, NH), 8.14 (d, 2H, *J*=8.1 Hz), 8.07 (d, 2H, *J*=7.5 Hz), 7.99 (d, 2H, *J*=8.1 Hz), 7.42 (t, 2H, *J*=7.8 Hz), 7.40 (d, 2H, *J*=7.8 Hz), 7.22 (d, 2H, *J*=7.8 Hz), 7.21 (s, 2H), 7.13 (t, 2H, *J*=7.5 Hz), 6.98 (t, 2H, *J*=7.5 Hz), 6.89 (t, 2H, *J*=7.5 Hz), 6.81 (s, 2H), 6.64 (d, 2H, *J*=7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 149.3, 148.7, 141.4, 141.2, 137.6, 136.7, 132.0, 129.1, 128.2, 128.0 (broad, 2C), 125.5, 124.2, 122.3, 120.7, 120.5, 120.3, 120.1, 110.8, 100.1, 66.0. mp 203–235°C (turns red). Anal. calcd for $C_{41}H_{26}N_2$: C, 90.11; H, 4.76; N, 5.13. Found: C, 89.67; H, 4.90; N, 5.18.
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