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Construction of Novel Ditopic Ligands Bearing Fused Polyaromatic and Alkyne Spacers

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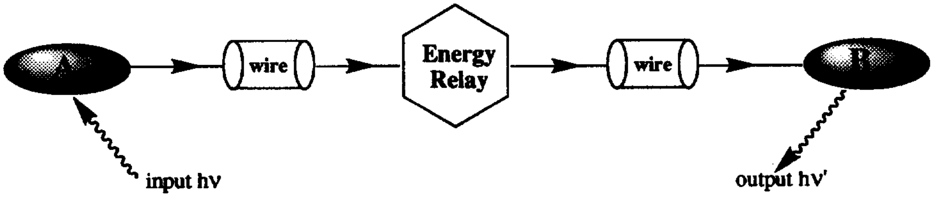
Abstract: We report the preparation of multi-component molecules based on ethynyl-substituted 2,2'-bipyridine and 2,2':6',6"-terpyridine derivatives and *para* substituted phenyl, naphtalene and anthracene moieties. The triple bonds play the role of a wire while the polyaromatic systems behave as an energy relay subunit. © 1997 Published by Elsevier Science Ltd.

In natural photosynthesis, complex arrays of antennae (pigments) collect the solar energy and convert it into the chemical potential that drives the chemistry of the photosynthetic machinery.[1] These processes are very fast, unidirectional and highly efficient. The pivotal processes involved in Nature have guided the Chemist in the design and construction of artificial systems which mimic the cascade of photochemical events.[2] We and others have found that alkyne modules are very useful to connect different luminophoric units and to effectively favour energy tunnelling.[3] Two archetypal examples are the molecular photonic wires[4] and the photoactive molecular-scale wires.[5] Both systems consists of an array of pigments in which absorption of a photon of visible light by an input chromophore at one end leads to emission of a photon by an output chromophore at the opposite end of the molecule. The quantum yield for energy migration from input to output is found to be very high.[6,7]

Here, we further implement the idea by introducing a polyaromatic energy relay within the conjugated system. We expect that the conjugated backbone will act as the energy migration channel after absorption of light energy by the input chromophore and the polyaromatic group as an energy *springboard* system. A representation of the overall process is shown in the Scheme below.



The excited-state triplet energy level of the transmission element could be modulated by the number of aromatic groups present in the *springboard* (from 353 kJ mol^{-1} in phenyl, to 255 in naphtalene and to 175 in anthracene).[8]

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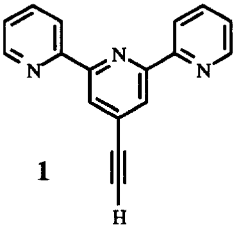
A related flexible and non conjugated supramolecular species containing fluorophores and an anthracene chromophore has recently been studied.[9]

The synthesis of the target molecules (**3** to **8**) combines modular building blocks (**1** and **2**) with dibromosubstituted derivatives using cross-coupling reaction similar to those used in the synthesis of multitopic ligands.[10]



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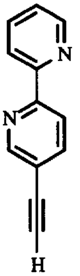

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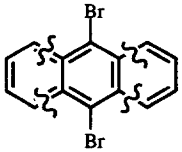
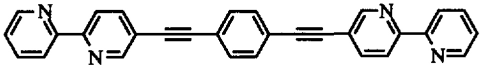


1,4-dibromobenzene
1,4-dibromonaphtalene
9,10-dibromoanthracene

These multi-component molecules were typically prepared on a 200 mg scale by reaction of 4'-ethynyl-2,2':6',2"-terpyridine **1**[11] (2.2 equiv.) or 5-ethynyl-2,2'-bipyridine **2**[12] (2.2 equiv.) with 1,4-dibromobenzene, 1,4-dibromonaphtalene[13] or 9,10-dibromoanthracene (1 equiv.), in *n*-$PrNH_2$ (base and solvent) under argon (Schlenk tube techniques) at 60°C, using $[Pd^0(PPh_3)_4]$ (6 mol%) as catalyst precursor.



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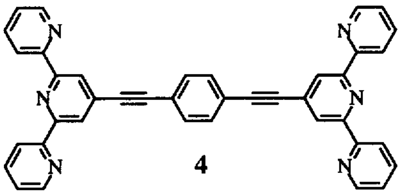

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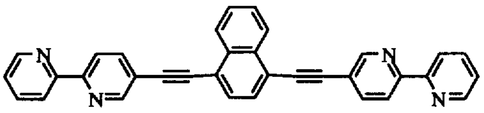

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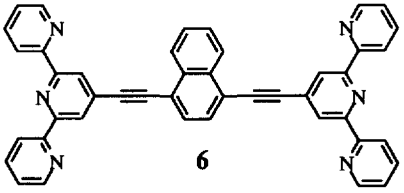

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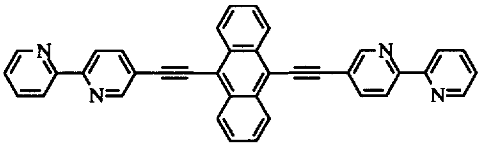

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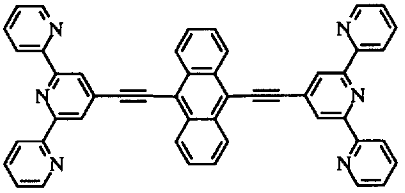

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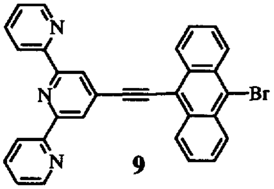
During the course of the reaction the desired pale-yellow (phenyl), deep-yellow (naphtalene) and orange (anthracene) ligands precipitate from the reaction mixture, driving the reaction to completion within two days. The pure compounds were obtained in excellent yields after purification and were characterized by classical techniques including elemental analyses. On the basis of spectroscopic evidence, the structures of the new multi-component molecules were unequivocally authenticated (see Table for selected data).

Product	Isolated Yield (%)	IR ($\nu_{C\equiv C}$, cm^{-1}) a)	UV-Vis λ nm, (ε, M^{-1}cm^{-1}) b)	Mass spectrum c)
3	92	not active	342 (80 000)	435.2
4	90	2217	292 (73 300); 375 (46 000)	589.3
5	90	not active	290 (31 200); 376 (76 100); 397 (55 400)	485.3
6	67	2206	290 (63 300); 426 (37 000)	639.3
7	46	not active	270 (87 700); 330 (41 300); 475 (45 400)	535.2
8	96	2200	284 (63 800); 495 (26 800); 517 (26 800)	689.2
9	50	2190	269 (122 000); 413 (26 700); 438 (28 400)	513.9
10	98	2191	276 (131 000); 452 (53 100); 479 (56 700)	612.3
11	97	2191	276 (97 000); 285 (97 400); 444 (45 400); 594 (61 900)	1225 [M-PF$_6$]
12	90	2187	269 (58 400); 283 (56 200); 481 (35 900); 605 (42 000)	1279.2 [M-2PF$_6$]

a) $\nu_{C\equiv C}$ stretching vibration measured in KBr pellets; b) π-π* absorption bands measured in CH_2Cl_2 or in CH_2Cl_2/trifluoroacetic acid (pH = 1.0) for compounds **4**, **6**, **8**; c) obtained by FAB$^+$ using *meta*-nitrobenzylalcohol as matrix and correspond to *m/z* [M+H]$^+$ until otherwise specified.

The straightforward synthetic method described here also allows the preparation of the monofunctionalized terpy/bromoanthracene compound **9**, which turned to be a very useful synthon for the stepwise preparation of the mixed ligands **10**. Obviously, this building block will be very useful for the future construction of multi-cascade intraspacer energy transfer relays based on anthracene/naphtalene or anthracene/azo systems.



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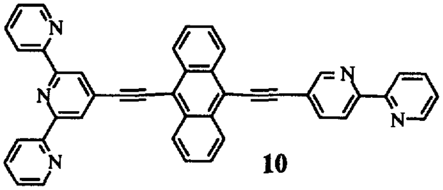

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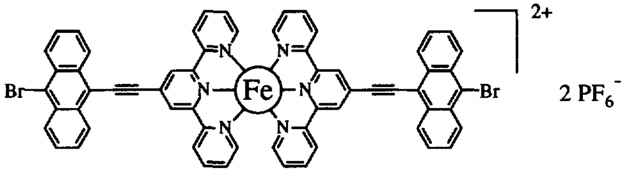
All these ligands exhibit as expected intense π-π * absorption in the near-UV region. The spectra show clearly the features of the bpy or terpy and phenyl, naphtalene or anthracene subunits. The iron(II) complexes **11** and **12** exhibit an intense MLCT absorption transition around 600 nm, which unambiguously indicates that the terpy domain in the mixed bpy/anth/terpy ligand **10** is complexed by the iron. Complexation of the bpy domain is less favorable and should lead to an MLCT transition at higher energy (ca. 530 nm), as indeed observed in $[Fe(bpy)_3]^{2+}$ or related complexes.[14,15]



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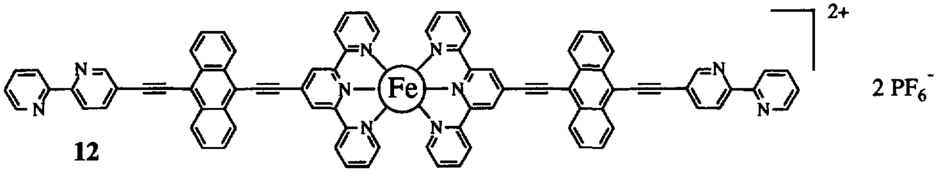

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The synthetic approach described here is a powerful method for the construction of stable ditopic ligands bearing five components (two chelating centres, two wires and one energy transfer module). These molecules are currently used to prepare luminophoric transition metal complexes. Detailed photophysical studies of their properties will be a fruitful area for model studies of energy transfer reaction in structurally well-defined and rigid molecular architectures.

References and Notes

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