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# Rigid rod-like molecular wires of nanometric dimension. Electronic energy transfer from a naphthyl to an anthracenyl unit connected by a 1,4-pentaphenylene spacer

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## Contents

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## Abstract

We have synthesized the multicomponent species **N–(ph)$_5$–A**, where a 1-naphthyl (**N**–) and a 9-anthryl (–**A**) units are connected by a 1,4-pentaphenylene rod-like spacer (–**(ph)$_5$**–). The overall length of the compound is 3.1 nm and the center-to-center distance between the naphthyl and anthryl units is 2.6 nm. The absorption and emission spectra of **N–(ph)$_5$–A** have been investigated in cyclohexane solution at 293 K and compared with those of model

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compounds of the component units. Emission spectra, fluorescence quantum yields and excited state lifetimes show that in **N–(ph)$_5$–A** the fluorescence of the naphtyl and oligophenyl units is completely quenched by energy transfer to the fluorescent excited state of the anthryl unit. The mechanism of the energy transfer process is discussed.

*Keywords:* Electronic energy transfer; Naphthyl; Anthracenyl; 1,4-Pentaphenylene spacer

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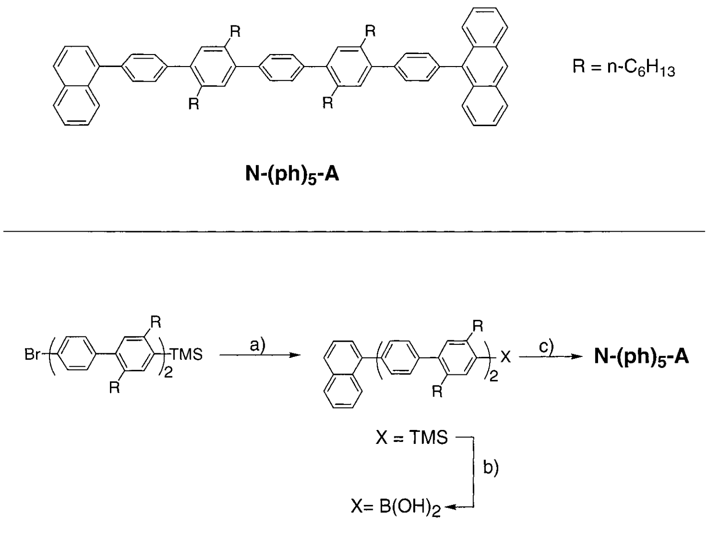
## 1. Introduction

The design of molecular-level devices and the bottom-up construction of miniaturized components capable of performing specific functions are important challenges facing modern chemistry [1]. A particularly interesting class of molecular-level devices is that capable to use photons as energy or information inputs (photochemical molecular devices) [1b]. An essential function that needs to be performed for the construction of photochemical molecular devices is the transfer of electronic energy over long distances and/or along predetermined directions [2,3]. In this regard, the spacer linking the photoactive units plays a fundamental role. When the spacer is not rigid (i.e. $-(CH_2)_n-$ chains), the geometry of the system is not defined. Rigid spacers are, therefore, by far more interesting. The role played by a spacer, however, is not only structural, since its chemical nature controls the electronic communication between the selected terminal units. Spacers that are too easy to oxidize or to reduce and/or possess low energy electronic levels are unsuitable because they can play the role of quenchers. On the other hand, aliphatic spacers do not allow sufficiently strong electronic interaction over long distances. Another important feature for a spacer is a modular nature [4], which allows changing distance without changing the electronic nature of the connection. For all these reasons oligophenylene rods [5] have attracted much interest as spacers [6–10], but their use has so far been limited to species containing a few phenylene units because of synthetic difficulties related to solubility problems. This difficulty, however, has recently been overcome by Schlüter et al. [11] by appending alkyl chains on the phenylene units.

Continuing our investigations on the study of energy-transfer processes in supramolecular systems, we have taken advantage of Schlüter's strategy to prepare the novel compound **N–(ph)$_5$–A** (Fig. 1), where a 1-naphthyl (**N**–) and a 9-anthryl (–**A**) units are connected by a 1,4-pentaphenylene-type spacer (–**(ph)$_5$**–) bearing alkyl chains. In this paper we report the excited state properties of **N–(ph)$_5$–A** and of its component units. The overall length of the compound is 3.1 nm and the center-to-center distance between the naphthyl and anthryl units is 2.6 nm. The results obtained are discussed with reference to those recently reported on energy transfer from $Ru(bpy)_3^{2+}$ to $Os(bpy)_3^{2+}$ units separated by oligophenylene spacers [12].



a) 1-naphthyl boronic acid, $Pd(PPh_3)_3$, 74%
b) $BBr_3$, $H_2O$, 55%
c) 9-(*p*-bromophenyl)anthracene, $Pd(PPh_3)_3$, 81%

Fig. 1. (a) Formulas of the investigated compounds and abbreviations used. (b) Schematic representation of the synthetic procedure.

## 2. Experimental

The rigid spacer TMS–$\mathbf{(ph)_5}$–Br (where TMS = trimethylsilyl) was synthesized following the procedure of Schlüter et al. [11]. The **N**–$\mathbf{(ph)_5}$–**A** compound was synthesized from the asymmetrically functionalized tetraphenyl as indicated at the bottom part of Fig. 1.

Suzuki cross-coupling [13] with commercially available 1-naphthylboronic acid and subsequent deprotection with boron tribromide afforded the boronic derivative after hydrolysis. Suzuki coupling with 9-(*p*-bromophenyl)anthracene [14] gave the **N**–$\mathbf{(ph)_5}$–**A** compound. The compound **N**–$\mathbf{(ph)_5}$–TMS was also prepared for comparison purposes. A description of the experimental procedure is given as supplementary material. The 1-phenylnaphthalene (**N**–**ph**) and 9-phenylanthracene (**A**–**ph**) reference compounds were commercial products (Aldrich). Experiments were carried out in air equilibrated cyclohexane solution using previously described equipment [8,12]. The concentration of the solutions was $1-2\times10^{-5}$ M. Under such conditions, bimolecular quenching processes can be ruled out because of the short excited-state lifetime of the fluorescent species (vide infra).

## 3. Results

The fluorescence data in cyclohexane at 293 K for naphthalene (**N**) [15], anthracene (**A**) [15], **N–ph**, **A–ph**, TMS–**(ph)**$_5$–Br, **N–(ph)**$_5$–TMS, and **N–(ph)**$_5$**–A** are given in Table 1 and the spectra of **N–(ph)**$_5$–TMS, **A–ph**, TMS–**(ph)**$_5$–Br, and **N–(ph)**$_5$**–A** are shown in Fig. 2.

As one can see, each one of the three separated component units of **N–(ph)**$_5$**–A** exhibits a strong fluorescence band. The fluorescence spectrum of the **N–(ph)**$_5$**–A** compound (Fig. 2(b)) shows an intense anthracene-type fluorescence band, whereas no band of the **N**–, –**(ph)**$_5$–, or **N–(ph)**$_5$– components is present. Quantitative fluorescence intensity measurements (using **A–ph** as a standard) [15] have also shown that in **N–(ph)**$_5$**–A** the quantum yield of the anthracene-type fluorescence does not depend on whether the excitation is performed on the **A**-based ($\lambda_{exc} = 365$ nm) or **N** and –**(ph)**$_5$-based ($\lambda_{exc} = 292$ nm and $\lambda_{exc} = 265$ nm) components. These results show that the complete quenching of the fluorescent excited states of the naphthalene and pentaphenylene-based components is accompanied by quantitative energy transfer to the lower lying anthracene-based fluorescent level. This is consistent with the fact that the lifetime of the **N–(ph)**$_5$**–A** fluorescence is much longer than that of Br–**(ph)**$_5$–TMS and **N–(ph)**$_5$–TMS, and close to that of **A** (see Table 1).

## 4. Discussion

To a first look, **N–(ph)**$_5$**–A** could be considered as made of a naphthalene and an anthracene chromophoric groups separated by a pentaphenylene-type spacer (Fig. 1). In this view, one would expect the occurrence of an energy-transfer process, with

Table 1
Photophysical data [a]

| | Es [b] (KJ mol$^{-1}$) | Φ [c] | τ [d] (ns) |
|---|---|---|---|
| **N** [e] | 385 | 0.19 | 9.6 |
| **A** [e] | 318 | 0.30 | 5.3 |
| **N–ph** | 379 | 0.37 [e] | 13 |
| **A–ph** | 301 | 0.41 [e] | 6.5 |
| Br–**(ph)**$_5$–TMS | 380 | 0.56 [f] | <1 |
| **N–(ph)**$_5$–TMS | 366 | 0.70 [f] | 1.1 |
| **N–(ph)**$_5$**–A** | 297 | 0.75 [g] | 4.0 |

[a] Air equilibrated cyclohexane solution, 293 K.

[b] Energy of the fluorescent excited state, estimated as indicated in Ref. [15].

[c] Fluorescence quantum yields, ±15%.

[d] Excited state lifetime.

[e] From Ref. [15].

[f] Standard: *p*-terphenyl in cyclohexane, $\phi = 0.77$, Ref. [15].

[g] Standard: **A–ph**.

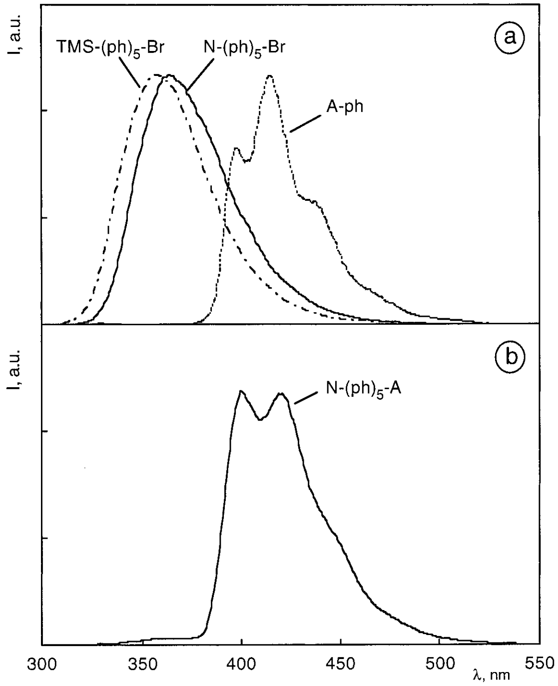


Fig. 2. Emission spectra in cyclohexane at 293 K of (a) TMS–**(ph)**$_5$–Br, N–**(ph)**$_5$–TMS, and **A**–**ph**; (b) N–**(ph)**$_5$–**A**.

the naphthalene unit playing the role of a donor and the anthracene one playing the role of an acceptor, mediated by the spacer via a superexchange mechanism [1b,16], as it happens, for example, in the case of the previously examined **Ru(bpy)**$_3^{2+}$–**(ph)**$_5$–**Os(bpy)**$_3^{2+}$ compound (Fig. 3(a)) [12,17].

The data reported in Table 1, however, show that in the case of **N–(ph)**$_5$**–A** the energy level of the bridge is, in fact, lower than that of the energy donor. Therefore, the **N–(ph)**$_5$**–A** system is somewhat more similar to the previously studied triad **Ru(bpy)**$_3^{2+}$**–A–Os(bpy)**$_3^{2+}$, in which a **Ru(bpy)**$_3^{2+}$ and **Os(bpy)**$_3^{2+}$ units are separated by an anthracene spacer (Fig. 3(b)) [18], where energy transfer occurs by a hopping mechanism [19]. In fact, the situation of **N–(ph)**$_5$**–A** is different also from that of the latter compound, since the energy levels of the donor (**N**) and of the bridge (**–(ph)**$_5$**–**) are very close in energy (Fig. 4) and therefore mixing of the states of the donor (**N–**) and the bridge (**–(ph)**$_5$**–**) components takes place, as indicated by (i) the red shift of the **N–(ph)**$_5$–TMS emission compared with that of **N** and TMS–**(ph)**$_5$–Br, and (ii) the much shorter lifetime of the **N–(ph)**$_5$–TMS excited state compared with that of the **N** and **N–ph** species.

Therefore, a more correct interpretation of the energy-transfer process that takes place quantitatively in **N–(ph)**$_5$**–A** is the following: the excitation energy is delocalized in the **N–(ph)**$_5$**–** moiety, as in a giant chromophore, and is then trapped (hopping step) by the anthracene chromophore. This behavior is reminiscent of that

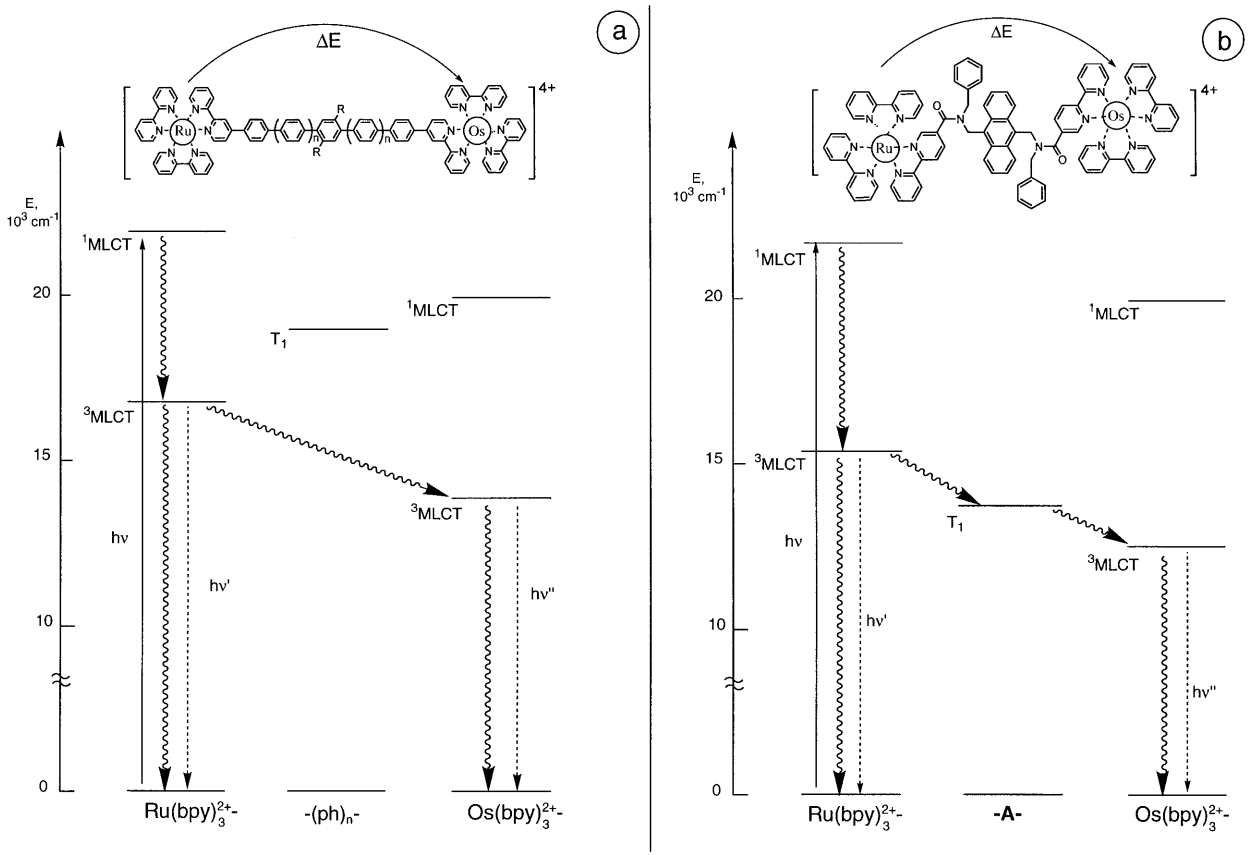


Fig. 3. Energy level diagrams for electronic energy transfer in (a) **Ru(bpy)$_3^{2+}$–(ph)$_5$–Os(bpy)$_3^{2+}$** [12], and (b) **Ru(bpy)$_3^{2+}$–A–Os(bpy)$_3^{2+}$** [19]. For more details, see text.

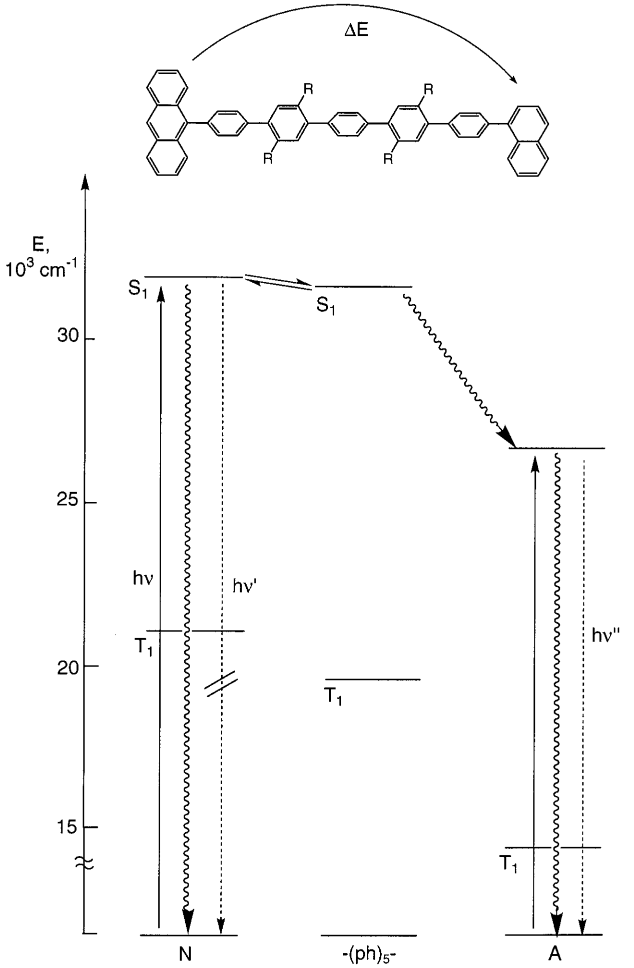


Fig. 4. Energy level diagram for electronic energy transfer in the **N–(ph)$_5$–A** compound. For more details, see text.

observed for photoinduced electron transfer across a conjugated bridge where, on increasing the bridge length, the energy of the LUMO orbital of the bridge approaches that of the locally excited electron donor unit (molecular wire behavior) [20].

## 5. Conclusion

The oligophenylene spacers are able to transfer electronic energy over long distances (see also Ref. [12]). Since light is going to play a major role in signal generation, processing, and storage, it is particularly important to design systems capable of performing photoinduced energy and electron transfer processes over long distances and/or along predetermined directions.

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