## Synthesis and Spectroscopic Properties of a Hexapyrenylbenzene Derivative<sup>†</sup>

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## ABSTRACT



In this paper, we present a synthetic approach to the first hexapyrenylbenzene starting from 4,5,9,10-tetrahydropyrene. Absorption and fluorescence spectroscopic measurements show strong and red-shifted fluorescence both from locally excited pyrene states and from the excitonic manifold of the aggregate.

Highly symmetrical, star-shaped molecules such as hexaarylbenzenes can be used to investigate basic aspects of energy transfer, delocalization, or storage in chromophore aggregates as they occur, e.g., in the natural light-harvesting systems LH I and LH II.<sup>1-4</sup> For this reason, we designed a model compound **8** which is based on the pyrene chromophore: six pyrenyl substituents are arranged in a regular manner and held together by a central benzene core. This simple model compound shall serve to explore the basic photophysical aspects of such 6-fold molecular arrangements.

Pyrenyl subchromophores were chosen because the photochemistry of pyrene is quite rich (excimer formation,<sup>5–7</sup> delayed fluorescence, and rather long fluorescence lifetimes) and well understood.<sup>8</sup>

In addition, hexaarylbenzenes have attracted interest in material science in recent years<sup>9–11</sup> for applications as lightemitting and charge-transport layers in OLEDs,<sup>12</sup> precursors

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 $<sup>^{\</sup>dagger}$  Dedicated to Prof. Dr. Manfred Christl on the occasion of his 65th birthday.

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for photoconductive polycyclic aromatic hydrocarbons,<sup>13–16</sup> and discotic liquid crystals.<sup>17</sup>

Molecular modeling of 8 without ester groups (see Figure 1) shows that owing to the pyrene H atoms in the 1, 3, 4,



Figure 1. Molecular modeling of 8 without ester functionalities.

and 10 positions the pyrenyl substituents adopt a propellerlike geometry in which the pyrenyl rings have a dihedral angel of ca. 58° to the central benzene ring.

In this context, it is essential that pyrene is bound in the 2 position to the central benzene ring because this minimizes direct orbital overlap with the benzene core because of the pyrene HOMO and LUMO having nodes through the 2 and 7 positions.18

Although most pyrene-derived chromophores are based on 1-substituted pyrene, substitution of pyrene in the 2 position represents a general problem because electrophilic substitution is usually strongly favored in the 1 position followed by substitutions in the 3, 6, or 8 position.<sup>19,20</sup> Thus, a direct access to 2,7-disubstituted pyrenes is almost impossible. Therefore, the synthesis of 2,7-substituted pyrenes requires an indirect route. The bridged biphenyl 1 can selectively be substituted by electrophiles in the 2 and 7 positions followed by back-oxidation to the corresponding pyrenes.<sup>21,22</sup>

In this communication, we present the synthesis of the hexapyrenylbenzene 8, which carries long alkylester groups in the 7 position for better solubility. 4,5,9,10-Tetrahydropyrene 1 was synthesized from pyrene according to a literature procedure.<sup>23,22</sup> Compound 1 was converted to 2,7dibromotetrahydropyrene following a modified bromination method of Harvey et al.,<sup>21</sup> who used a solution of 4,5,9,10tetrahydropyrene in acetic acid (Scheme 1).

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Subsequently, 2,7-dibromotetrahydropyrene 2 was monolithiated in the key step with *n*-BuLi at -90 °C and reaction with octylchloroformate led to the ester 3 in one step in moderate to good yields.<sup>24</sup> The ester **3** was easily oxidized with 2 equiv of DDQ to give 4 (Scheme 2).<sup>23</sup>



The reaction of 4 with trimethylsilylacetylene (TMSA) in a standard Hagihara/Sonogoshira coupling vielded 5 in 60%<sup>25</sup> Deprotection of **5** with TBAF in THF gave **6** in quantitative yields (Scheme 3).<sup>26</sup>



The resulting terminal acetylene 6 was then coupled with 4 in the same coupling procedure used before to obtain  $7.^{25}$ Workup of this tolan compound is difficult, owing to high insolubility, but washing of the crude product with cold dichloromethane gave 7 that was pure enough for the last conversion step (Scheme 4).

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Finally, a conventional alkyne trimerization reaction of **7** with  $Co_2(CO)_8$  provided the desired compound **8** in 25% yield. The low yield is mainly caused by two precipitation steps which were needed for purification (Scheme 4). Figure 2 shows the MALDI-ToF mass spectrum of **8**.



Figure 2. MALDI-ToF mass spectrum of 8.

In Figure 3, the UV/vis spectrum together with the corresponding emission spectrum in dichloromethane are dis-



**Figure 3.** UV/vis spectrum (red) and fluorescence spectrum (black) of **8** in dichloromethane. Deconvolution of the fluorescence spectrum is in blue and green.

played. Table 1 shows the absorption and emission maxima and the corresponding extinction coefficients of **8**.

The absorption spectrum shows the typical allowed L<sub>a</sub> band at 28 800 cm<sup>-1</sup> and the much weaker forbidden L<sub>b</sub> band at 25 100 cm<sup>-1</sup>. Both bands display vibronic structure and are distinctly shifted to lower energy compared to ethyl pyrene-2-carboxylate ( $L_a = 30\ 000\ cm^{-1}$ ,  $\epsilon = 4.5 \times 10^4\ M^{-1}$ cm<sup>-1</sup>,  $L_b = 25500$  cm<sup>-1</sup>,  $\epsilon = 2 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> in cyclohexane).<sup>27</sup> Furthermore, the spectrum is dominated by an intense unresolved band at 35 700 cm<sup>-1</sup>. This band is at an energy similar to that for the B<sub>b</sub> and B<sub>a</sub> bands of ethyl pyrene-2-carboxylate (B<sub>b</sub> = 35 500 cm<sup>-1</sup>,  $\epsilon$  = 2.5 × 10<sup>4</sup>  $M^{-1} \text{ cm}^{-1}$ ,  $B_a = 38\ 000\ \text{cm}^{-1}$ ,  $\epsilon = 7 \times 10^4\ \text{M}^{-1}\ \text{cm}^{-1}$ ). All bands are much more intense than those of ethyl pyrene-2carboxylate, but they do not quite reach the 6-fold intensity as expected. In addition, there is a broad and unresolved band at ca. 21 500 cm<sup>-1</sup> which is absent in ethyl pyrene-2carboxylate and which we tentatively assign to an excitation in the excitonic manifold of the pyrene hexaaggregate. In this way, 8 is unlike pyrene which shows a concentrationdependent excimer fluorescence but no corresponding absorption band. The emission spectrum of 8, peaked at 24 100 cm<sup>-1</sup>, also shows a vibronic fine structure but is much less resolved than that of the pyrene parent compound. At the low-energy side, there is a broad and unresolved shoulder

**Table 1.** Absorption and Emission Maxima and ExtinctionCoefficients of 8 in Dichloromethane

	$\lambda_{max}(nm)$	$\tilde{\nu}_{\rm max}~({\rm cm}^{-1})$	$\epsilon \; (\mathrm{M}^{-1} \: \mathrm{cm}^{-1})$
absorption	280	35700	348000
	347	28800	178000
	398	25100	8400
	465	21500	1200
emission	415	24100	
	483	20700	

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which is more intense in polar solvents (e.g., acetonitrile) than in moderately or apolar solvents. The emission spectrum is independent of the concentration such that excimer formation between two molecules of 8 could be excluded. This broad emission band (given in blue in Figure 3) of 8 is more obvious after deconvolution of the emission band into four equally broad (900 cm<sup>-1</sup>) Gaussian bands (given in green in Figure 3) according to the vibrational structure which then yields the fifth band as the difference to the experimental spectrum. This fifth band is lower in energy than the lowest-energy absorption band and might be due to the emission from the excitonic manifold (or two adjacent pyrene moieties), whereas the vibrationally resolved band is due to the emission from locally excited pyrene chromophores. In contrast, the model monomer 7-phenyl-pyrene-2-carbonic acid octylester does not show any concentrationdependent excimer fluorescence. Thus, the red-shifted emission appears to be a unique property of the hexameric aggregate. Further spectroscopic characterizations (i.e., time-resolved measurements), particularly to prove the origin of the blue band, are in progress and will be disclosed elsewhere.

In conclusion, we described a synthetic approach for the synthesis of hexapyrenylbenzene chromophores which shows strong and red-shifted fluorescence both from locally excited pyrene states and from the excitonic states of the aggregate.

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**Supporting Information Available:** Synthetic procedures and characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org. OL0618196

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