Optical Spectroscopy of Isolated and Aggregate Hexabenzocoronene Derivatives: A Study of Self-Assembling Molecular Nanowires

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The low, medium, and high concentration luminescence and luminescence-excitation spectra for alkyl substituted hexa-*peri*-hexabenzocoronene (HBC$-$C$_{8,2}$) and hexa(4-*n*-dodecylphenyl) substituted hexa-*peri*-hexabenzocoronene (HBC$-$PhC$_{12}$) are presented. A study of the concentration dependence of the optical properties of these self-assembling molecular nanowires, in the low to medium concentration regime, associates the spectrum at $\sim$10^{-13} M with the isolated molecule and indicates that previously published spectra of HBC's by others were the product of aggregation phenomena. The insertion of an exo-phenyl group between the HBC core and the alkyl side chains, as in HBC$-$PhC$_{12}$, was found not to extend the conjugation but did increase the inhomogeneous broadening of the isolated molecule luminescence. The continued presence of HBC$-$PhC$_{12}$ isolated molecules, at high concentration, implies that HBC$-$C$_{8,2}$ aggregates are thermodynamically more stable than HBC$-$PhC$_{12}$ aggregates. This is further supported by the calculated values for the Coulombic ground-state binding energy (W), the Coulombic excited state$-$ground-state interaction energy (W') and the resonance interaction energy (β) for the aggregates of both derivatives (HBC$-$C$_{8,2}$: $W \approx 0$ eV, $W' \approx 0.16$ eV, and $\beta = 0.27 \pm 0.02$ eV; HBC$-$PhC$_{12}$: $W \approx 0$ eV, $W' \approx 0$ eV, and $\beta = 0.23 \pm 0.02$ eV). In the excited state, the exo-phenyl groups of HBC$-$PhC$_{12}$ were found to enhance the aggregate intermolecular vibronic coupling despite sterically hindering the full aggregation in the ground state. In conclusion, the spectroscopic properties of both derivatives were found to be very sensitive to aggregation at low concentration and strongly correlated to the observed macroscopic physical properties.

1. Introduction

Processes of energy minimization, through molecular interaction, could be used to construct molecular nanowires, molecular transistors, and other necessary components required for highly integrated, nanoscale electronic circuitry. With no external assistance, these processes can induce molecules to self-assemble in a passive and efficient way. Permanent dipole$-$permanent dipole interactions (Coulombic), permanent dipole$-$induced dipole interactions (induction), and flickering dipole$-$induced dipole interactions (dispersion or van der Waals) can all contribute to the attractive potential. A discotic molecule such as hexa-*peri*-hexabenzocoronene (HBC), with a small permanent dipole moment and a large polarizability, offers a well defined, self-arranging system that can be studied and modified to help develop our understanding of the aggregation processes.

Presented here are two very similar compounds: alkyl substituted HBC (HBC$-$C$_{8,2}$)[1] and hexa(4-*n*-dodecylphenyl) substituted HBC (HBC$-$PhC$_{12}$).[2] The chemical structures of the two derivatives are given in Figure 1. The slight modification of the HBC$-$PhC$_{12}$ may seem trivial but in fact gives rise to significant differences in the electronic and physical properties of the assembled materials.

Because of the strong $\pi-\pi$ interactions, substituted HBC molecules self-assemble into highly ordered columnar stacks[3] (see schematic in Figure 1c) which are further arranged in various 2D arrays in the solid state. Figure 1c shows an idealized situation where the disks are parallel and *perfectly rotationally staggered*. X-ray diffraction measurements[1] have demonstrated that the cores of HBC$-$C$_{8,2}$ and other alkyl substituted HBCs are tilted and crystallized (no rotation or translation) relative to the columnar axis at room temperature. Upon heating above a given thermotropic phase transition, the disks become perpendicular to the columnar axis and gain mobility to spin about the axis. Because of the exo-phenyl groups of HBC$-$PhC$_{12}$ which suppress crystallization, these latter features are observed already at room-temperature. Some of these physical properties, as will be shown later, are strongly correlated to the optical spectroscopy results presented here.

The large aromatic core of the HBC derivatives ensures an extensive $\pi-\pi$ overlap of neighboring molecules in the columnar aggregate stacks. This is demonstrated by the high charge carrier mobilities of alkyl substituted HBC and HBC$-$PhC$_{12}$ films, studied by van der Craats[4] et al. In the solid crystalline phase, a charge carrier mobility in excess of 0.1 cm^2 V^{-1} s^{-1} has been reported, falling to half this value in the liquid-crystalline hexagonal columnar phase. HBC derivatives also display the largest charge mobility observed for a discotic liquid crystal[5] and have successfully been used in highly efficient organic solar cells.[6]

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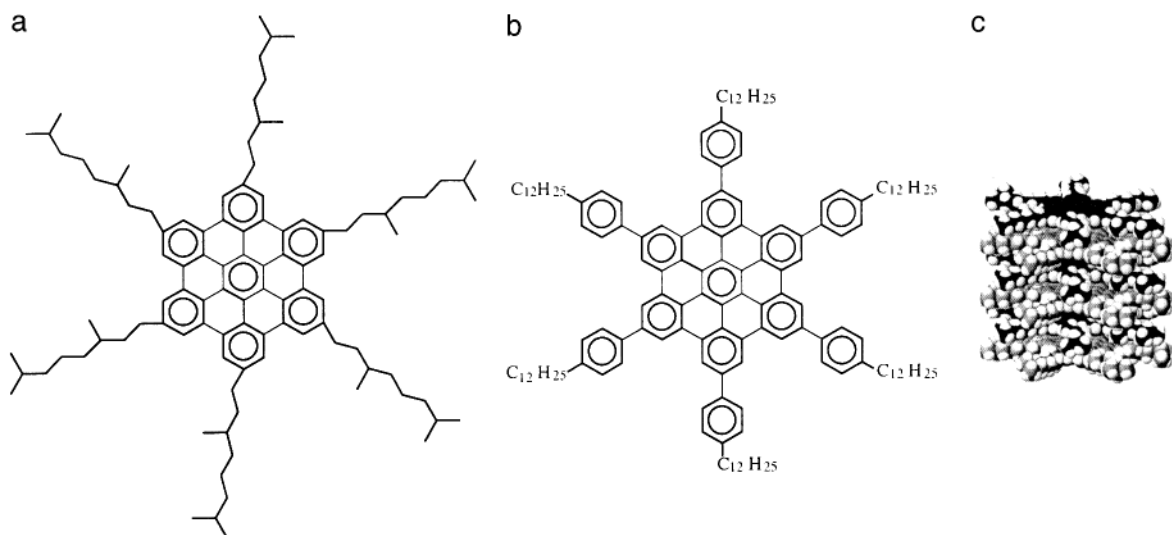§ Max-Plank-Institut für Polymerforschung.
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Figure 1. (a) Alkyl substituted HBC (HBC−C$_{8,2}$, Mr = 1364.21) and (b) hexa(*para-n*-dodecylphenyl) substituted HBC (HBC−PhC$_{12}$, Mr = 1989.12). (c) Schematic showing an example of HBC−C$_{8,2}$ stacking (in this possible arrangement each successive molecule in the stack is rotated by 30°).

The high solubility of these alkyl- and alkyl-phenyl-substituted HBCs has made it possible to measure the optical properties of the materials at low concentrations, yielding information on the isolated, nonaggregated molecules. In this study, the luminescence and luminescence-excitation spectra of the materials' isolated molecules are recorded at very low concentration (10^{-15}–10^{-9} M), where the high photoluminescence quantum efficiency of the isolated molecules makes it possible to measure the spectrum with a standard luminescence spectrophotometer.

It will be shown that such low concentrations are required to observe the spectroscopic signature of the unaggregated molecules and that the effects of aggregation may be seen at concentrations as low as 10^{-9} M. It should be noted that the average optical response of a large number of isolated molecules and/or aggregates is recorded and *not* the optical response of a single molecular entity or single molecular aggregate. This differentiates these measurements from the field of single molecule spectroscopy. The term "isolated molecule" is used in this paper to describe molecules in dilute solution, whereas the term "*noncoupled* molecule" is used to describe isolated molecules found at high concentration where aggregates are thermodynamically more favorable.

2. Experimental Section

The HBC materials in powder form, as synthesized by Fechtenkötter[1,2] et al., were weighed and dissolved, into approximately 10^{-3} M solutions in spectroscopic grade toluene. Each solution was then sonicated using a sonic tip to break up the large aggregates. A 1.66 mL volume was taken and diluted by one-third by adding 3.32 mL of toluene. This sample was then sonicated and the procedure repeated using the diluted sample as the starter until 24 solutions of progressively lower concentrations were made up for each material. The sample concentrations thus spanned a range from 10^{-3} M to approximately 10^{-15} M. The fluorescence properties of the samples were then measured using photoluminescence and excitation techniques. Each photoluminescence and excitation spectra measured was carried out in solution in 1 cm quartz sample cuvettes using a Perkin-Elmer LS 50 B luminescence spectrometer.

At concentrations below 10^{-7} M, standard absorption photometers are not as optically sensitive as luminescence spectrometers (it is easier to detect a small amount of light than it is to detect a small decrease in light intensity). Nevertheless, the absorption spectra for each derivative, at medium and high concentration,[7] was measured (results not shown) and found to match the excitation spectra of each peak in the luminescence spectra, thus proving that there is only one chromophore per molecule present. In all cases, excitation spectra will be presented because of their superior signal-to-noise ratios.

Throughout the measurements of the excitation and luminescence spectra, there was only one instance when two species (or two chromophores) where observed in solution. This was at high concentration when *noncoupled* molecules of HBC−PhC$_{12}$, in addition to aggregates, were found to be in solution (this will be shown in section 3.2.2.). In general, all luminescence spectra are obtained from exciting the molecules at the excitation maximum, and all luminescence-excitation spectra were measured by detecting the fluorescence at the luminescence maximum.

3. Results and Discussion

3.1. Isolated Molecules. At the lowest concentration explored (3×10^{-15} M), any isolated nonaggregated molecules present have an average intermolecular distance of approximately 80 μm. This separation is expected to be sufficient to prevent any attractive intermolecular interactions that could lead to an increase in the rate of aggregation. In practice, the aggregation process is controlled by random molecular collisions, and at these low concentrations, collisions are expected to be rare. This results in a negligible number of aggregates present compared to the number of isolated molecules present.

In the low concentration range between 10^{-15} and 10^{-9} M, the profiles of both excitation and luminescence spectra were not observed to vary significantly. The low concentration (1×10^{-13} M) luminescence and luminescence-excitation spectra shown in Figure 2 are representative of this range (the spectral features are listed in Table 1). This would suggest that there is at most limited aggregation occurring at these concentrations.

The low concentration molecular excitation and luminescence spectra of both derivatives are very similar. Two broad excitation peaks are observed for both derivatives (the lower energy peak, around 3.1 eV, is responsible for the material's luminescence). The luminescence spectra should therefore be a mirror image of this low energy excitation feature for noninteracting mol-
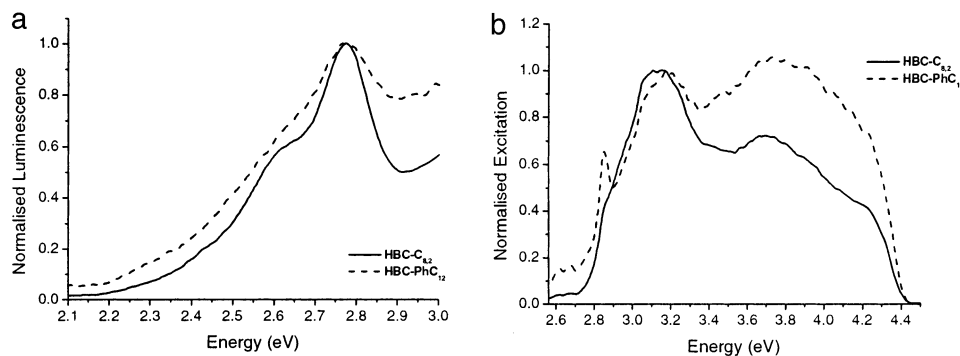
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Figure 2. (a) Normalized (intensity) low concentration luminescence and (b) normalized (intensity) low concentration luminescence-excitation (at 1×10^{-13} M). The excitation peak at 2.85 eV and lower energy features are spectrometer related artifacts prominent only at low concentrations.

TABLE 1: Excitation and Luminescence Peak Positions and fwhm's for Low Concentration Solutions of Both Derivatives (at 1×10^{-13} M)

spectra	derivative	peak maximum (eV)	peak fwhm (eV)	comment
excitation	HBC$-$C$_{8,2}$	3.14 ± 0.02	0.56 ± 0.02	luminescent peak
		3.70 ± 0.03		
	HBC$-$PhC$_{12}$	3.17 ± 0.03	0.58 ± 0.04	luminescent peak
		3.73 ± 0.06		
luminescence	HBC$-$C$_{8,2}$	2.776 ± 0.003	0.323 ± 0.005	
	HBC$-$PhC$_{12}$	2.776 ± 0.004	0.45 ± 0.04	

ecules. In the case of the HBC$-$PhC$_{12}$ derivative, the PhC$_{12}$ side-chains have caused both excitation peaks to blue-shift by ~0.03 eV relative to the HBC$-$C$_{8,2}$. This implies that, although both broad excitation peaks probably arise from a superposition of many electronic transitions, the phenyl group has caused a general change, suggesting that there is, to some extent, electronic coupling throughout the HBC$-$PhC$_{12}$ molecule. However, the fact that the phenyl groups do not induce a red-shift reduces the likelihood that the exo-phenyl groups are extending the π conjugation. As these phenyl groups are free to rotate, they can only contribute to the electronic system when a phenyl group lies in the π-conjugated plane. Because the rotations of the six exo-phenyl groups are most likely incoherent, they only contribute to the inhomogeneous broadening of the system. In addition, by normalizing the higher energy excitation peaks (around 3.7 eV), the HBC$-$PhC$_{12}$ excitation spectrum was found to be slightly broader.

The low concentration luminescence (at 1×10^{-13} M) is shown in Figure 2a for both materials. In each case, these spectra display a high energy peak at approximately 2.8 eV with a shoulder at 2.6 eV (see Table 1). However, in comparison to the excitation spectra, the HBC$-$PhC$_{12}$ luminescence is noticeably broader than that of the HBC$-$C$_{8,2}$. This suggests that the addition of phenyl groups has broadened the excited state emission, possibly by broadening the vibronic-rotational bands. Furthermore the Stokes shifts for both derivatives at low concentration are similar: 0.36 ± 0.02 (HBC$-$C$_{8,2}$) and 0.39 ± 0.03 eV (HBC$-$PhC$_{12}$), the slightly lower value in the former suggesting that the relaxation of the HBC$-$PhC$_{12}$ molecules may be greater, possibly because of solvent effects on the phenyl groups.

Estimating the relative photoluminescence efficiency from the luminescence magnitudes gives a value for the phenyl derivative of roughly 20% that for the HBC$-$C$_{8,2}$ (this is also the reason for the noisier signal). This can potentially be explained by the efficient vibronic coupling of the phenyl group in HBC$-$PhC$_{12}$ to the phenyl group in the toluene solvent.[8] The rotating phenyl groups, although only contributing to the π-bond system when they are in the same plane as the HBC core, will always be coupled vibronically to the core via the σ bond. The large overlap between the vibronic spectra of toluene and of

the exo-phenyl groups in HBC$-$PhC$_{12}$ ensures an efficient vibronic coupling between them. The photoexcitation is more likely to decay via the fastest route; thus, the efficient phonon coupling to the solvent enhances the nonradiative pathway and leads to a decrease in the overall photoluminescence efficiency.

It is evident that the low concentration luminescence and luminescence$-$excitation spectra of HBC$-$C$_{8,2}$ are significantly different to those of HBC-*tert*-C$_4$ (tertiary butyl groups) and HBC$-$C$_{12}$ published by Biasutti et al.[9] Likewise, the HBC$-$PhC$_{12}$ spectra are also different to those published previously, suggesting that the side chains are not responsible for the discrepancy in spectra. In fact, Biasutti's spectra resemble the medium concentration spectra presented here. It is therefore more likely that the difference in concentration, at which the luminescence and luminescence$-$excitation spectra were recorded, is responsible.

Although the low concentration luminescence and luminescence$-$excitation spectra are indicative of the presence of isolated molecules, these spectra alone do not prove that the isolated molecules are uniquely being observed. However, as will be shown in the next section, the change and shift in spectra from low concentration to medium concentration strongly suggests that the isolated molecules of HBC$-$C$_{8,2}$ and HBC$-$PhC$_{12}$ have in fact been observed in the region of 10^{-13} M.

3.2. Aggregates. An aggregate is formed when two or more single molecules interact strongly enough that spontaneous separation becomes energetically unfavorable. The probability of this interaction is concentration dependent and is therefore not significant at sufficiently low concentration. As the concentration is increased, the isolated molecules in solution are depleted in favor of aggregates; however, changes to the optical spectra indicative of aggregates only become observable at concentrations above 10^{-9} M for these materials (at which point the isolated molecular spectrum starts to be replaced by that of the aggregate spectrum). Aggregates generally have much lower luminescence quantum efficiencies;[10] however, the higher concentration of aggregates typically compensates[11] making them observable.

3.2.1. Medium Concentration. Figure 3, parts a and b, shows the luminescence and luminescence$-$excitation spectra respectively for HBC$-$C$_{8,2}$ and HBC$-$PhC$_{12}$ solutions at 1.7×10^{-8}
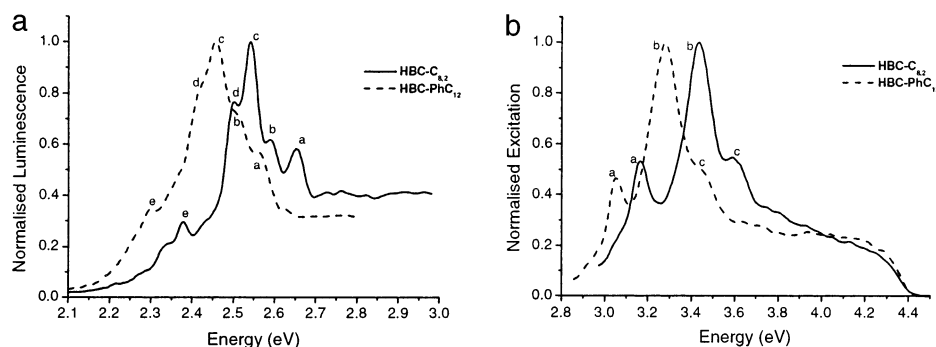
Figure 3. (a) Normalized medium concentration luminescence and (b) normalized medium concentration excitation spectra (at 1.7×10^{-8} M).
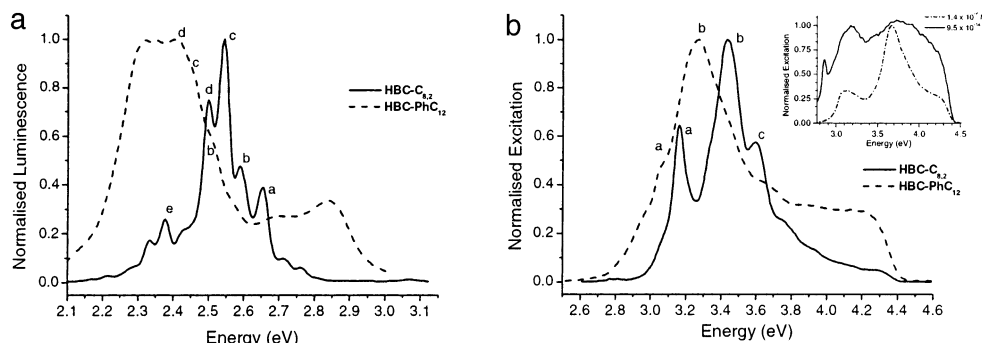

Figure 4. (a) Normalized high concentration luminescence and (b) normalized high concentration excitation (at 1.4×10^{-6} M). Inset: Comparison of excitation collected at 2.69 eV of isolated molecules at 1×10^{-13} M (black line) and *noncoupled* molecules at 1.4×10^{-6} M (dashed dotted line).

TABLE 2: Excitation and Luminescence Peak Positions and fwhm's for Medium Concentration Solutions of Both Derivatives (at 1.7×10^{-8} M)

spectra	derivative	peak maximum (eV)	peak fwhm (eV)	comment
excitation	HBC$-$C$_{8,2}$	3.434 ± 0.005	0.21 ± 0.01	peak b Figure 3b
	HBC$-$PhC$_{12}$	3.279 ± 0.005	0.21 ± 0.01	peak b Figure 3b
luminescence	HBC$-$C$_{8,2}$	2.541 ± 0.005	0.10 ± 0.01	peak c Figure 3a
	HBC$-$PhC$_{12}$	2.457 ± 0.005	0.21 ± 0.01	peak c Figure 3a

M (medium concentration). There is a marked difference to the low concentration spectra, with such concentration dependence clearly indicating the presence of aggregates.

For both materials, the structure of the excitation spectrum between 3.8 and 4.4 eV is very similar to the equivalent region in the low concentration spectra. The continued presence of this broad featureless region is indicative of the remaining presence of some isolated molecules at medium concentration. In the lower energy region, the HBC$-$C$_{8,2}$ medium concentration excitation maximum at 3.434 eV is blue-shifted by 0.29 eV with respect to the low concentration, isolated molecule excitation maximum at 3.14 eV (see Figure 3b peak b and Table 2). In comparison, the HBC$-$PhC$_{12}$ medium concentration excitation maximum at 3.279 eV (see Figure 3b peak b and Table 2) is only blue-shifted by 0.11 eV from the low concentration excitation maximum at 3.17 eV. This is less than half the blue-shift of the HBC$-$C$_{8,2}$ excitation maximum.[12] In addition, two subsidiary peaks at higher and lower energy with respect to the excitation maximum have appeared at medium concentration (see peaks a and c in Figure 3b). The energetic mismatches, between the peak positions of the excitation spectra of both derivatives, arise from the addition of the phenyl groups to the side-chains of the HBC core that in turn has led to changes in the aggregates' morphology.

For both materials, the luminescence peak positions have red-shifted significantly with respect to the low concentration luminescence. These positions are given in Figure 3a and Table 2. In both cases, significant vibronic structure has appeared compared to the low concentration spectra. This is more evident

in the case of the HBC$-$C$_{8,2}$ spectrum as it is less broadened than the HBC$-$PhC$_{12}$ medium concentration luminescence (see Figure 3a and Table 2). This sharper emission may suggest that the conformation of the ground electronic vibrationally excited state ($\phi_i{}^*$) of HBC$-$C$_{8,2}$ at 1.7×10^{-8} M is more ordered than for HBC$-$PhC$_{12}$. As the electronic de-excitation (or transition) occurs on a shorter time scale than structural reorganization, we can expect the nuclear positions to be the same before and after the electronic de-excitation. Therefore, we expect the excited electronic vibrationally relaxed state (ϕ_f) to have an equivalent structure to the $\phi_i{}^*$ state.[13] The Stokes shift is the sum of the relaxation energies involved in changing from the vibrationally excited state to the vibrationally relaxed state (i.e. the change from $\phi_f{}^*$ to ϕ_f and $\phi_i{}^*$ to ϕ_i). The similar Stokes shifts of the aggregates (0.89 ± 0.01 eV for HBC$-$C$_{8,2}$ and 0.83 ± 0.01 eV for HBC$-$PhC$_{12}$) therefore suggest a similar energy relaxation process for both derivatives.

3.2.2. High Concentration. At higher concentration (1.4×10^{-6} M), there are further differences in the luminescence and luminescence$-$excitation spectra of both derivatives (see Figure 4, parts a and b, and Table 3). In the low energy region of the excitation spectrum, the spectral features remain for the most part unchanged relative to the medium concentration spectra. Although the Franck$-$Condon maxima positions stay the same, a noticeable sharpening of vibrational features for the HBC$-$C$_{8,2}$ material has been observed. In contrast, the equivalent features in the HBC$-$PhC$_{12}$ spectrum have broadened. The high energy features, associated with the isolated molecule, remain in the HBC$-$PhC$_{12}$ excitation spectrum but have practically

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TABLE 3: Excitation and Luminescence Peak Positions and fwhm's for High Concentration Solutions of Both Derivatives (at 1.4×10^{-6} M)

spectra	derivative	peak maximum (eV)	peak fwhm (eV)	comment
excitation	HBC−$C_{8,2}$	3.434 ± 0.005	0.23 ± 0.01	peak b Figure 4b
	HBC−PhC_{12}	3.269 ± 0.007	0.43 ± 0.01	peak b Figure 4b
luminescence	HBC−$C_{8,2}$	2.543 ± 0.005	0.08 ± 0.01	peak c Figure 4a
	HBC−PhC_{12}	2.40 ± 0.01	0.29 ± 0.01	peak c Figure 4a

CHART 1: (a) Stacking of Transition Dipole Moments and (b) the Electronic Transitions of the Monomer and Dimer for H Aggregates (Dipole Allowed Transitions, Solid Line; Dipole Forbidden, Dashed Line)
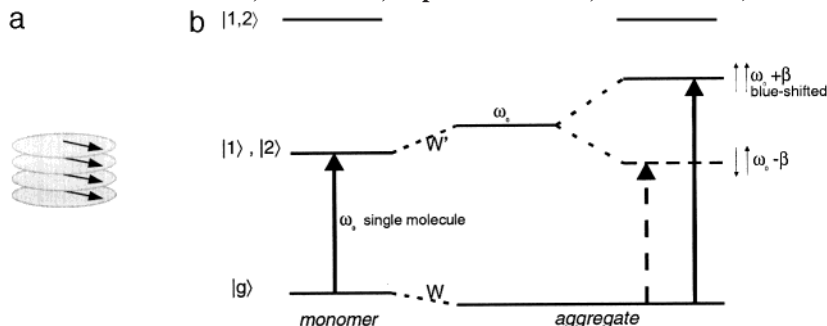
disappeared from the HBC−$C_{8,2}$ spectra. This is indicative of a more complete aggregation process in the latter case.

With an increase in concentration from 10^{-8} to 10^{-6} M, the overall HBC−PhC_{12} excitation has broadened a further ∼87% and its luminescence has broadened by ∼38%. Likewise, the HBC−$C_{8,2}$ excitation fwhm has also increased by ∼10%, but its luminescence has narrowed by ∼20%. This suggests that for both materials the ϕ_i* state and the ϕ_f state conformation is more ordered than the ground electronic vibrationally relaxed state (ϕ_i) and the excited electronic vibrationally excited state (ϕ_f*) conformation. The ratio of the fwhms of these two conformations was found to be concentration and derivative dependent. With the increase in concentration from 1.7×10^{-8} to 1.4×10^{-6} M this ratio was reduced by ∼27% for HBC−$C_{8,2}$ aggregates and increased by ∼26% for HBC−PhC_{12} aggregates. This indicates that any disorder introduced by the increase from medium to high concentration was only evident for the HBC−PhC_{12} aggregates whereas the HBC−$C_{8,2}$ aggregates actually increased in order. Interestingly, at high concentration, peak a is appreciably sharper than peaks b or c. The significance of this will be discussed in the next section.

Although the HBC−$C_{8,2}$ luminescence spectrum has narrowed slightly for the high concentration sample, its spectral profile has not been greatly affected. The HBC−PhC_{12} spectral profile, however, has undergone a significant and unexpected change relative to the medium concentration spectra. The luminescence spectrum for this material (given in Figure 4a) clearly shows that there are in fact two species contributing to the luminescence spectrum of the HBC−PhC_{12}. The features from 2.1 to 2.6 eV are most likely due to aggregate emission, whereas the features from 2.6 to 3.0 eV can be attributed to the luminescence of *noncoupled* molecules of HBC−PhC_{12}. To confirm the distinct nature of these species, a luminescence−excitation spectrum was collected at 2.69 eV (see inset Figure 4b). This spectrum displays a similar profile to the luminescence-excitation spectrum for the isolated molecule in the 1×10^{-13} M sample. This strongly suggests the presence of *noncoupled* molecules even in the 1.4×10^{-6} M solution. There is, however, a change in the relative peak heights from low to high concentration. This is almost certainly due to changes in the environment of the *noncoupled* versus isolated HBC−PhC_{12} molecule.

At 1.4×10^{-6} M, the luminescence peak at 2.45 eV of the HBC−PhC_{12} aggregates is no longer the only maximum (see

Figure 4a). The peak at 2.32 eV becomes more dominant with increasing concentration even though the excitation profile of the HBC−PhC_{12} does not vary with concentration. This is significant, as only the ϕ_f and ϕ_i* state conformation has been affected by the increase in concentration.

3.2.3. Discussion. The single disklike molecules are made up of a graphitic core surrounded by a number of aliphatic side-groups. The preferred aggregation of the single molecules is to self-assemble into columnar stacks (i.e., nanowires), but the optimal arrangement is not a straightforward face-to-face stacking; instead, a staggered and displaced arrangement,[14] which is constrained by the side-chains, is favored (see schematic in Figure 1c). However, it must be noted that, in solution and at room temperature, the molecules making up the aggregate are free to rotate about the columnar axis.

The high polarizability and small permanent dipole moment of the large centrosymmetric aromatic core ensures that the dispersion interaction, and not the Coulombic (electrostatic) interaction, is the most dominant term in the total interaction energy. The centrosymmetric geometry of the HBC core ensures that the *electronic transition* dipole moments of the single molecules point along-the-plane of the molecule (see Chart 1a). Columnar stacking of the single molecules will therefore form H aggregates.[15]

An aggregate is essentially a collection of strongly coupled single molecules. The degree and nature of the molecular interaction can be described by three factors: the Coulombic binding energy of the aggregate ground state W (negative for dimers and larger aggregates, and positive for excimers), the Coulombic interaction energy W' of the excited state of one molecule with the ground state of another, and finally the resonance *or transfer* interaction term β. The resonance interaction term will determine the degree of splitting of the aggregate energy levels. For H aggregates, assembled from parallel stacked molecules with a centrosymmetric transition dipole moment, we expect $\beta > 0$ as the moments should lie parallel to each other (see Chart 1, parts a and b). Therefore, the higher of the two dimer exciton states is dipole allowed and has the larger oscillator strength. The result will be a blue-shift of the aggregate excitation spectrum with respect to the isolated molecule spectrum.

The increase in concentration of isolated molecules, from 10^{-13} to 10^{-8} M, alone cannot explain the dramatic change in the luminescence and luminescence−excitation spectra ob-

served: a new species must be responsible. Formed at medium concentration, H aggregates will generally blue-shift the excitation spectrum. Using the shift of the Franck−Condon excitation maximum observed, from low to medium concentration, the relative magnitude of the resonance interaction term for both derivatives can be estimated. Initially assuming the values for W and W' for each compound are similar, then the β value scales with the observed blue-shift. Calculated in this way, the HBC−$C_{8,2}$ aggregates have a relatively larger β value than the HBC−PhC_{12} aggregates ($\sim$1.6 times larger).

The collective behavior of excitons in an aggregate leads to exchange narrowing[16] of the absorption and emission bands relative to the isolated molecule. A decrease in fwhm of $\sim$63%, from low to medium concentration, is observed for the excitation spectra of both HBC−C_8 and HBC−PhC_{12} indicating the presence of aggregates. But why is peak a in Figure 4b significantly sharper than other peaks in the excitation spectrum of HBC−C_8? It turns out, that the dipole-allowed state, peak b in Figure 4b, is lifetime broadened as the exciton can quickly decay to the lower lying, dipole-forbidden state, peak a. This labels peak a, for the first time, as the dipole-forbidden state. Also, qualitatively speaking, the oscillator strength of peak a is significantly lower than that of peak b, adding further evidence that peak a is the dipole-forbidden state. This makes it possible to measure the resonance interaction term directly. The values for 2β measured using the simplistic dipole−dipole approximation are 0.27 ± 0.02 eV for HBC−$C_{8,2}$ and 0.23 ± 0.02 eV for HBC−PhC_{12}. A possible explanation for the slightly larger value for HBC−$C_{8,2}$ is that the HBC−$C_{8,2}$ molecules in the aggregate stack are better aligned or are held closer together, thus ensuring a more extensive mixing of states between neighboring molecules (i.e., a larger overlap between the molecular π-bond systems). More significantly, the HBC−$C_{8,2}$ aggregates seem to have a larger Coulombic interaction ($|W| + |W'| = 0.16 \pm 0.04$ eV) compared to the HBC−PhC_{12} aggregates (negligible energetic shift). This interaction is also known as the "crystal shift" in the case of molecular bulk crystals and describes the difference in ω_0 for a *noncoupled*/isolated molecule compared to a single molecule as part of an aggregate. The Coulombic binding energy W can be estimated from the point-dipole approximation $W = \mu^2/R^3$, where R is the intermolecular plane distance ($\sim$3.5 Å) and μ is the permanent dipole moment. HBC−$C_{8,2}$ has a very small permanent dipole moment $\mu \approx 0.06$ D[17] and thus has an almost negligible shift of ≈ -0.05 meV. This implies that W' (because of the high polarizability) is the more dominant of the two Coulombic interactions. The large positive value for W' of the HBC−$C_{8,2}$ molecules is possibly due to the greater cohesion and smaller intermolecular distance increasing the magnitude of the Coulombic term and hence increasing ω_0. On the other hand, the more loosely bound HBC−PhC_{12} molecules have a similar ω_0 to when *noncoupled*/isolated. This would suggest that the HBC−PhC_{12} molecules in the stack behave in a fashion more similar to the nonaggregated case. However, despite W being negligible for both derivatives, aggregates do form. This is because the van der Waals (dispersion) interaction, and not the Coulombic interaction, is the dominating force binding the aggregates together (for both molecules, the permanent dipole moments are small and the polarizabilities are large). The larger Coulombic and resonance interactions of the HBC−$C_{8,2}$ aggregates would manifest themselves physically by the aggregates being more robust and stable, as confirmed by X-ray diffraction measurements[2] (HBC−$C_{8,2}$ is known to be crystalline at room temperature where HBC−PhC_{12} is a liquid crystal).

Biasutti et al.[8] have previously reported that from the alkyl substituted HBCs investigated HBC-*tert*-C_4 does not form aggregates and the broadening of the HBC−C_{12} is indicative of an aggregation phenomenon. The spectra presented in Biasutti's paper are remarkably similar to the medium concentration spectra presented here. This suggests that the material studied by Biasutti had already aggregated. This is supported by the fact that the lowest concentration explored was 10^{-7} M.

Further evidence that aggregates have formed can be found in the shift of the Franck−Condon maximum from low to medium concentration, but first the excitation and luminescence transitions must be labeled.[18] The excitation spectra of HBC−$C_{8,2}$ and HBC−PhC_{12} in Figure 3b are similar in profile but not identical. A straightforward and simple method of comparing and labeling the vibronic structures, of two very electronically and vibronically similar derivatives, is to offset the energy axis of one spectrum to overlap as many peaks as possible with the other spectrum. Any energetic mismatches between the overlapping peaks will be due to the addition of the exo-phenyl group on HBC−PhC_{12} and its subsequent effect on the aggregate. Furthermore, the medium concentration luminescence spectra in Figure 3a are in fact the mirror images of their respective excitation in Figure 3b. The detailed structure of the HBC−$C_{8,2}$ medium concentration luminescence, when matched to its mirror image excitation spectrum, enables the vibronic transitions for each peak in the spectrum to be labeled. The excitation and luminescence maxima of the aggregates for both materials are the 0−1 and 1−0 transitions, respectively. This is expected from an aggregate as the effective mass has increased, shifting the Franck−Condon maximum from the 0−0 transition to the 0−1 or 1−0 transition.[19] This is further evidence that the spectra observed at this concentration belong to the aggregates and not the isolated molecules.

Interestingly, at high concentration, an inconsistency between the Franck−Condon maxima of the HBC−PhC_{12} excitation and luminescence arises (compare Figure 4, parts a and b). The Franck−Condon maximum for the high concentration excitation is the 0−1 transition, whereas the luminescence Franck−Condon maximum is the 4−0 transition. This can be explained if, at high concentration, the aggregates' ϕ_f and $\phi_i{}^*$ conformation increases the vibronic coupling in the stack (assisted by the presence of the phenyl groups) so that the overall aggregate nuclear mass increases and therefore shifts the Franck−Condon maximum to the 4−0 transition. This is despite the fact that these phenyl groups sterically hinder the coupling of aggregates in the molecular electronic ground state conformation (making HBC−PhC_{12} a liquid-crystal in the electronic ground state).

The enhanced vibronic coupling nevertheless has not increased the electronic order of the HBC−PhC_{12} columnar aggregates [the fwhm values for this derivative are still larger than the values for the HBC−$C_{8,2}$ aggregates (see Table 3)]. The HBC−$C_{8,2}$ at medium concentration (1.4×10^{-6} M), without the bulky phenyl groups, is more inclined to form well-ordered stacks in the ground electronic vibrationally relaxed state (ϕ_i) conformation and especially so in the excited electronic vibrationally relaxed state (ϕ_f) conformation.

The addition of a phenyl group to the side-chains has produced some interesting effects. The phenyl groups do not contribute to the rest of the molecule electronically, but they do vibronically: the π-conjugation is no more extended in HBC−PhC_{12} than it is in HBC−$C_{8,2}$ (there was no red-shift in the isolated molecule excitation). The phenyl groups also seem to sterically hinder full aggregation, yet they manage to increase the vibronic coupling of the molecule to other molecules and

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to the toluene surrounding it. These seemingly contradicting results can only be realized if, on average, the phenyl side-groups in the aggregate stack lie at an angle to the HBC plane. In this manner, they are still physically coupled to the coronene core but the π systems of the phenyl group and the coronene do not overlap substantially, so they are electronically decoupled.

With the ground electronic vibrationally relaxed state (ϕ_i) conformation of the HBC$-$PhC$_{12}$ molecule sterically hindering aggregation, at 10^{-6} M, there exists a thermodynamic equilibrium between individual molecules binding and separating from the stack. This behavior is consistent with the liquid-crystalline behavior reported of HBC$-$PhC$_{12}$. The isolated molecules in solution not bound to the columnar stack are thus *noncoupled* molecules, surrounded by columnar aggregates, but not correctly aligned to bind to the stack. The difference in relative peak heights between the isolated molecule (at 10^{-13} M) and the *noncoupled* molecule excitation spectra (see inset of Figure 4b) can be attributed to changes in the environment of the exposed π bond system: the elimination of solvent effects and possible dampening of the low energy $\pi$$-$$\pi$* transition by the proximity of the columnar stacks. The presence of these *noncoupled* molecules at high concentration is further proof that the isolated molecular spectra of both HBC derivatives were indeed observed at low concentration.

4. Conclusions

The new synthesis of highly soluble HBC derivatives[1,2] has made it possible to measure the excitation and luminescence spectra at very low concentrations and to therefore observe the isolated molecules spectroscopically.

The insertion of phenyl groups between the pending alkyl side-chains and the aromatic core of HBC$-$PhC$_{12}$ does not affect the extent of the π-conjugation but does reduce the photoluminescence yield of the isolated molecules. It also significantly changes the physical and electronic properties of the aggregates formed: the results for HBC$-$PhC$_{12}$ aggregates point toward a pseudo-liquid-crystalline behavior in the ground state and an increase of the intermolecular vibronic coupling in the photo-excited state.

Likewise, the sharpening of the HBC$-$C$_{8,2}$ aggregate excitation and luminescence spectra, although mostly through exchange narrowing, shows an increase in stack order with concentration, which would follow through to the solid state, whereas an increase in HBC$-$PhC$_{12}$ aggregates' size seems to lead to more disorder.

The observation of the dipole-allowed state and dipole-forbidden state enable the molecular interaction of the aggregates to be assessed. The measured values for W, W', and β agree with a system comprised of highly polarizable, closely assembled molecules with a low permanent dipole moment and therefore support the idea that the aggregates are indeed observed at concentrations above 10^{-9} M. From this, it therefore follows that the low concentration spectra can be attributed to isolated molecular entities in solution. This idea is further supported by the similarity of the excitation spectra at low concentration to that of the *noncoupled* molecules found at high concentration.

The coronene family of compounds are very suitable class of materials for studying aggregation effects. The high purity and 2-D shape makes an interesting molecule easier to study and will hopefully help us understand the transition from 1-D charge transport to the bulk transport properties.

A more detailed analysis of the vibronic and rotational structure of the aggregates of both derivatives at different concentrations up to solid state will be given in a further paper, also including a complete study of the concentration dependence of the optical properties of the isolated molecules and aggregates formed.

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(11) The overall intensity increases making them observable.

(12) This blue-shift is not strictly correct, as the single molecule's excitation maximum is the 0−0 transition and the aggregate's excitation maximum is the 0−1 or higher transition. However, the relative change is nevertheless still meaningful; that is, the HBC$-$C$_8$ blue-shift is $\sim$1.64 times greater than HBC$-$PhC$_{12}$ blue-shift.

(13) The relaxed electronic excited state (ϕ_f) and unrelaxed electronic ground state (ϕ_i*) have the same structural conformation as electronic transitions occur in $\sim$10^{-15} s, whereas nuclear motions typically occur in $\sim$10^{-13} s. Most electronic transitions are therefore completed before the nuclei have altered their spatial position to accommodate the new charge distribution, so the transitions are termed "vertical" or "Franck$-$Condon transitions". This relaxation of the nuclear positions is responsible for the Stokes shift.

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