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Synthesis of J-Aggregating Diben[α,j]anthracene-Based
Macrocycles
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Abstract: Several fluorescent macrocycles based on 1,3-butadiyne-bridged dibenz[α,j]anthracene subunits
have been synthesized via a multistep route. The synthetic strategy involved the initial construction of a
functionalized dibenz[α,j]anthracene building block, subsequent installation of free alkyne groups on one
side of the polycyclic aromatic framework, and a final cyclization based on a modified Glaser coupling
under high-dilution conditions. Photophysical studies on three J-aggregated macrocycles revealed the formation
of J-aggregates in thin films, as well as in concentrated solid solutions (polysobutylen matrix), with peak
absorption and emission wavelength in the range of λ = 460–480 nm. The characteristic red-shifting of
the J-aggregate features as compared to the monomer spectra, enhancement in absorption intensities,
narrowed linewidths, and minimal Stokes shift values, were all observed. We demonstrate that improvements
in spectral features can be brought about by annealing the films under a solvent-saturated atmosphere,
where for the best films the luminescence quantum efficiency as high as 92% was measured. This class
of macrocycles represents a new category of J-aggregates that due to their high peak oscillator strength
and high luminescence efficiency have the potential to be utilized in a variety of optoelectronic devices.

Introduction
Shape-persistent macrocycles have received much attention
in the field of materials science, particularly in the area of
nanoscale architectures.1 The first macrocycle featuring two
unfunctionalized anthracenes linked by 1,3-butadiyne bridges
was reported in 1960, but due to the lack of modern synthetic
and characterization methods, the nature of the resulting material
was not rigorously elucidated.2 Following little interest in such
systems over the next four decades, reports of anthrylene-
ethylene oligomers and macrocycles have surfaced in the past
5 years.3 However, the molecular rigidity and lack of solubilizing
groups resulting in the reported compounds having poor
solubilities in common solvents. To create a class of molecules
that could have potentially interesting photophysical and materi-
als properties, we embarked on the design of conjugated macrocycles
based on rigid dibenz[a,j]anthracene units bridged
by butadiyne π-linkers. This was a logical choice since aryleneethylenylene and 1,3-butadiyne linkages are frequently
used in conjugated systems (e.g., polymers) for their ability to
maintain rigidity and π-conjugation.4 The polycyclic aromatic
motifs are commonly seen in other areas of materials science,
notably in the fields of discotic liquid crystals and graphitic
materials.5 By employing various modern synthetic transforma-
tions, it was possible to introduce numerous functionalities (e.g.,
side chains) into the structure to give better solubility and
processability. In particular, bulky 4-alkoxyphenyl substituents
located near the middle of the macrocycles serve several
purposes: (1) as synthetic handles to allow for the facile
electrophilic cyclizations6 used to establish the dibenz[a,j]an-
thracene framework, (2) as solubilizing groups, and most
importantly, (3) as a source of steric hindrance to bring about
twisting of the π-system. Such distortion of the rigid framework
by steric bulk has been known to induce slipped stacking
arrangements,7 resulting in aggregate structures with unique
optical properties. Similar slipped structures are also known
in nature: for example, the arrangement of J-aggregated chlorophyll
chromophores is crucial to the light-harvesting efficiency of

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photosynthetic systems. Using natural photosystems as a guide and inspiration, researchers have found ways to emulate this J-aggregate design in various porphyrins and perylene bisimides. More recently, the laboratories of Frank Würthner have also successfully implemented the rational synthesis of several J-aggregated systems using supramolecular design principles. Ever since their serendipitous discovery in 1936, J-aggregates have been of great theoretical interest because they display coherent, cooperative phenomena like superradiance and giant oscillator strength, a consequence of their electronic excitation being delocalized over several molecules. Besides being theoretical curiosities, J-aggregates also have a myriad of practical applications, such as their use as organic photoconductors, photopolymerization initiators, and nonlinear optical devices, as well as the emerging applications such as the recently demonstrated critically coupled resonators and strongly QED coupled microcavity LEDs.

Herein, we report the synthesis and characterization of a series of J-aggregating macrocycles based on functionalized dibenz[a,j]anthracene fragments linked at the 6- and 8-positions by a pair of 1,3-butadiyne bridges, in which the ring interior can be viewed as an octadehydro[18]annulene system. The results of their photophysical studies are also detailed.

Results and Discussion

Synthesis. Macrocycles 6a and 6b were prepared in six steps from the previously reported dibromide 1. Subjecting the dibromide to a double Suzuki coupling with 4-alkylphenylboronic acids afforded terphenyl derivatives, which were then converted to the required 6,8-diiododibenz[a,j]anthracenes via a double iodonium-induced electrophilic cyclization. Numerous attempts to convert the diiodide to the bis-acetylene 5 via Sonogashira and Castro–Stephens reactions proved unsuccessful, instead resulting in complex, recently demonstrated critically coupled resonators and strongly QED coupled microcavity LEDs.

Scheme 1. Synthesis of Macrocycles 6a and 6b
undefined mixtures. However, an indirect method involving a lithiation/carbonylation sequence to give 4, followed by Corey–Fuchs homologation, successfully afforded dialkyne 5. Owing to the sterically encumbered environment of the reaction centers, dialdehyde 4 was always accompanied by the formation of monoaldehyde byproduct 13. Separation of the two could however, be easily achieved by column chromatography. Finally, an oxidative coupling utilizing conditions previously developed in our group was performed, furnishing macrocycles 6a and 6b in reasonable yields.

The synthesis of macrocycle 12 (Scheme 2) involved a similar sequence of transformations employed in the preparation of 6a and 6b, with the exception that the bis-alkoxyterphenyl 7 could only be converted to the desired diiodide 9 in two steps, via a skeletal rearrangement of the structurally intriguing 8, using modifications of known reactions. A second alkoxy-based macrocycle bearing branched farnesol-derived side chains was also synthesized in a manner analogous to 12, with its existence confirmed by MALDI-TOF. Unfortunately, this fourth and final macrocycle could not be satisfactorily separated from a trimeric byproduct even after repeated column chromatography and attempted fractional recrystallizations. In addition to the three macrocycles, compound 15 (the acyclic analogue of 6a) was also prepared to study the effect of the number of bridges on the photophysical properties. This was made in three steps (Scheme 3) starting from monoaldehyde 13, which is a byproduct isolated during the purification of dialdehyde 4a.

The above-mentioned target compounds were characterized by 1H NMR, 13C NMR, high-resolution mass spectrometry (MALDI-TOF), UV−vis, and fluorescence spectroscopy. In the 1H NMR spectra of the macrocycles, the two protons located within the ring were found to be shifted downfield (δ ≈ 9.5 ppm) as a result of van der Waals deshielding brought about by steric interactions. The lack of any upfield shift of those internal protons implies the absence of a ring current in these systems (i.e., no diatropic effect observed). Brief polarized optical microscopy experiments were also performed on the macrocycles in hope of finding liquid crystalline behavior as well, but the compounds had extremely high melting points (between 200 and 330 °C) and were also observed to decompose and discolor at those elevated temperatures.

**Photophysical Studies.** A SPEX fluorolog, with dual monochromators, was used to collect photoluminescence (PL) and photoluminescence excitation (PLE) spectra. The instrument is wavelength and intensity calibrated, and it compensates for variations in excitation intensity by monitoring the incident optical power level. In PL measurements, the 6a films were optically excited at a wavelength λ = 375 nm. For PLE spectra,

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emission at $\lambda = 508$ nm was collected. Figure 1 shows the UV–vis absorption and fluorescence spectra of the four compounds in chloroform. Macrocycles 6a and 6b displayed essentially identical spectral profiles, with absorption and emission maxima occurring at around 440 and 455 nm, respectively. Changing the peripheral alkyl groups to alkoxy chains (e.g., 12) resulted in a slight bathochromic shift, with the spectral shape remaining similar otherwise. The spectra of the acyclic 15 differed somewhat from the macrocycles, which was expected due to the major structural difference. Its absorption spectrum was blue-shifted relative to the others, possibly due to reduced conjugation resulting from the absence of the second diyne linker. A much larger Stokes shift was also observed, which could indicate reduced rigidity, once again as a result of having only a single linker. Fluorescence quantum yields of the compounds were measured against quinine sulfate in 0.1 N H$_2$SO$_4$ (Table 1). The three macrocycles in chloroform solution showed fairly high quantum yields between 0.40 and 0.50, whereas the singly bridged 15 had a lower value of 0.35.

To test for the presence of J-aggregates, we investigated the thin film photophysics of the macrocycles. As 6a was synthesized in the largest quantity, films of this compound were studied in greatest detail. The initial films were produced by spin-coating a fairly concentrated (5 mg/mL) toluene solution of 6a on to glass or quartz coverslips (18 × 18 mm$^2$). Fortuitously, the first few films showed promising UV–vis absorption features consistent with J-aggregates (Figure 2).

Compared with the solution spectrum, the 6a film spectrum shows an aggregate absorption peak at 467 nm (red-shifted by (23 ± 1) nm from the solution). Even more notable is the high intensity and narrow line width of this peak (J-band), which dominates all other spectral features. This is in stark contrast to the solution spectrum, in which the peak at 443 nm shows much lower intensity than those between 300 and 360 nm (absorptions due to pendant $p$-alkoxyphenyl moieties). Normalizing the solution and film absorbances at 340 nm, the enhancement in the peak intensity (at 467 nm) relative to the other spectral features becomes evident (Figure 2). The bathochromic shift and the strong intensity of the aggregate peak,

**Table 1. Photophysical Properties of 6a, 6b, 12, and 15**

<table>
<thead>
<tr>
<th>compound</th>
<th>absorption max (nm)</th>
<th>emission max (nm)</th>
<th>quantum yield, $\Phi_F$</th>
<th>extinction coefficient (M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>443</td>
<td>456</td>
<td>0.45</td>
<td>90141 (at 443 nm)</td>
</tr>
<tr>
<td>6b</td>
<td>443</td>
<td>456</td>
<td>0.43</td>
<td>63569 (at 443 nm)</td>
</tr>
<tr>
<td>12</td>
<td>448</td>
<td>461</td>
<td>0.47</td>
<td>79113 (at 448 nm)</td>
</tr>
<tr>
<td>15</td>
<td>395</td>
<td>440</td>
<td>0.35</td>
<td>38206 (at 395 nm)</td>
</tr>
</tbody>
</table>

**Figure 1.** Normalized absorbance (solid lines) and emission (dotted lines) spectra of 6a, 6b, 12, and 15 in chloroform.

**Figure 2.** Absorption spectra of 6a, solution (blue line) vs film (red line), normalized to the absorbance at 340 nm.
are photophysical characteristics of J-aggregates. From the emission spectra of the 6a films we find the Stokes shift to be only 4 nm (Figure 3), versus 13 nm in solution phase. Such minimal Stokes shift is also consistent with the existence of J-aggregates. It is notable that the fluorescence band is a mirror image of the low-energy edge of the J-band absorption.

We also find that it is possible to spin-coat films of 6a that did not display a J-band. These less strongly absorbing films could be produced when the spin rate (of the spin-coating process) was high (e.g., 4000 rpm), a lower concentration (<2 mg/mL) of 6a in solvent was used, or when a more volatile solvent (e.g., THF) was employed. The use of these parameters provided for less-than-favorable conditions for aggregate formation. However, when these ‘nonaggregated’ (i.e., monomeric) films were then subjected to conditions conducive to aggregate formation, the typical J-aggregate spectral features were found to emerge with time. This was achieved by vapor-annealing the films in a solvent chamber saturated with toluene vapor for 45 min, and then retrieving them for spectral (UV–vis) reacquisition. It can be seen (Figure 4) that the vapor-annealing, which should result in more ordered thin films, precipitates the appearance of the highly intense J-band, confirming that molecular organization was indeed important in producing the desired J-aggregate photophysics. When the volatile THF is used as the spin-casting solvent (particularly with low 6a concentration) the resulting films lacked J-aggregate features. However, J-aggregate features can be recovered when these films are placed in a solvent chamber containing THF vapor (Figure 4).

Similar photophysical experiments were also performed on films of the two longer-chained macrocyclic analogues 6b and 12. In both cases, the films are cast from THF solutions of the macrocycles and subsequently annealed under THF vapor for 45 min. UV–vis data are acquired before and after the annealing process, and the spectra of 6b and 12 are shown in Figure 5. The spectra of the preannealed films did not show J-bands, but these appeared in both cases upon annealing. Therefore, the results obtained with 6b and 12 were analogous to those of 6a, suggesting that the doubling of chain length of the peripheral alkylalkoxy groups had little effect on the photophysics, be it in solution or in the film-state. Similar J-aggregate photophysics could not be observed with the noncyclic 15, implying that the aggregate formation may require approximate molecular planarity (steric hindrance in the noncyclic 15 produces a larger deviation from planarity, since the two dibenzanthracene subunits are less constrained). It is likely that J-aggregation of these polycyclic aromatics in the solid-state relies on π–π stacking interactions that could be disrupted if the nonplanarity became too pronounced.

Additional experiments examining the photophysics of 6a as a function of concentration were also undertaken. A series of films were spin-coated using 6a solutions (polyisobutylene matrix/chlorobenzene as solvent) of varying concentrations, and their photoluminescence spectra, excitation spectra, and fluorescence lifetimes were measured. Chlorobenzene was chosen as it provided for optimal miscibility of 6a, polyisobutylene, and solvent. When a film containing a very low concentration of 6a (i.e., 0.0005 mg in a 1 mL solution of 40 mg/mL polyisobutylene (PIB) in chlorobenzene) was used, its emission peak was at 455 nm (Figure 6), identical to that observed in solution spectra. As the amount of 6a used in the spin-coating process was increased to 0.002 mg/mL of PIB/chlorobenzene,

aggregate peaks began to emerge at 470 nm with a shoulder at 500 nm, while the 455 nm “monomer” peak diminished. A further increase in 6a concentration to 0.005 mg/mL resulted in further reduction in the 455 nm peak, so that at 0.02 mg/mL, the monomer peak can no longer be observed, at which point the emission spectrum begins to resemble those obtained with J-aggregate films. To determine PL QY, we compared the PL counts from the 6a film to a thin film standard of known QY, accounting for relative differences in absorption strength of the films. The standard was a thin film of thickness 75 nm of the small molecule tris-(8-hydroxyquinolinato)aluminum (Alq3). The Alq3 film was prepared by thermally evaporating recrystallized Alq3 in ultra high vacuum (growth pressure below 10^-6 Torr) onto a quartz substrate that was carefully solvent cleaned and oxygen plasma treated to remove trace impurities. The published QY for Alq3 in thin film is 32% ± 2%.29 We erred on the side of caution and used a value of QY = 30% for our calculations.

The emergence of a red-shifted narrower line width optical transition at higher 6a concentrations, the corresponding reduction in lifetime, and increase in quantum yield of aggregates as compared to monomers are indicative of J-aggregate formation.27 In J-aggregates, strong coupling between the monomer transition dipoles produces a new cooperative molecular state. The coupling results in a new optical transition called the J-band, when the interaction strength exceeds the monomeric dephasing processes.28 The interaction between monomeric transition dipoles lowers the overall energy of the cooperative state; hence, the J-band absorption/fluorescence is red-shifted relative to that of the monomer. In the J-aggregate state, multiple molecules coherently couple, the number being denoted by N, and the J-aggregate exciton delocalizes over all of them. Typically referred to as a superradiance phenomenon since it is a coherent process. The interaction strength exceeds the monomeric dephasing processes.29 Coherent coupling among the N, molecules leads to the acceleration of the radiative rate of the J-band states by a factor of V/N, relative to that of the monomer. In the J-aggregate state, multiple molecules coherently couple, the number being denoted by N, and the J-aggregate exciton delocalizes over all of them.29 Coherent coupling among the N, molecules leads to the acceleration of the radiative rate of the J-band states by a factor of N relative to the monomer, which translates into shorter excited-state lifetime and higher PL QY. The radiative rate enhancement is typically referred to as a superradiance phenomenon since it is a coherent process.

**Table 2. Fluorescence Lifetimes of 6a (Solutions and Films) at Different Concentrations**

<table>
<thead>
<tr>
<th>concentration (mg/mL)</th>
<th>lifetimes (bimodal) (ns)</th>
<th>state</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>1.7 (100%)</td>
<td>solution (PhCl)</td>
</tr>
<tr>
<td>0.02</td>
<td>1.7 (100%)</td>
<td>solution (PhCl)</td>
</tr>
<tr>
<td>0.2</td>
<td>1.8 (100%)</td>
<td>solution (PhCl)</td>
</tr>
<tr>
<td>0.0005</td>
<td>1.3 (99.9%)</td>
<td>4.8 (0.1%) film</td>
</tr>
<tr>
<td>0.002</td>
<td>0.2 (96.7%)</td>
<td>1.3 (3.3%) film</td>
</tr>
<tr>
<td>0.005</td>
<td>0.3 (96.6%)</td>
<td>1.2 (3.4%) film</td>
</tr>
<tr>
<td>0.01</td>
<td>0.3 (97.4%)</td>
<td>1.0 (2.6%) film</td>
</tr>
<tr>
<td>0.02</td>
<td>0.2 (98.1%)</td>
<td>1.1 (1.9%) film</td>
</tr>
<tr>
<td>0.05</td>
<td>0.6 (84.5%)</td>
<td>1.5 (15.5%) film</td>
</tr>
<tr>
<td>0.10</td>
<td>0.4 (82.7%)</td>
<td>1.4 (17.3%) film</td>
</tr>
<tr>
<td>0.20</td>
<td>0.4 (94.9%)</td>
<td>1.4 (5.1%) film</td>
</tr>
<tr>
<td>2.00</td>
<td>0.2 (97.4%)</td>
<td>0.7 (2.6%) film</td>
</tr>
</tbody>
</table>

± 6% for the monomeric film to ΦJ = 92% ± 8% for the aggregate films. To determine PL QY, we compared the PL peaks from the 6a film to a thin film standard of known QY, accounting for relative differences in absorption strength of the films. The standard was a thin film of thickness 75 nm of the small molecule tris-(8-hydroxyquinolinato)aluminum (Alq3). The Alq3 film was prepared by thermally evaporating recrystallized Alq3 in ultra high vacuum (growth pressure below 10^-6 Torr) onto a quartz substrate that was carefully solvent cleaned and oxygen plasma treated to remove trace impurities. The published QY for Alq3 in thin film is 32% ± 2%.29 We erred on the side of caution and used a value of QY = 30% for our calculations.

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caused by coherent exciton coupling, though in J-aggregates the mechanism for the coupling is near-field Coulombic interactions while in classic superradiant systems, the origin is interference effects in the spontaneous light emission process. 

Since the radiative rate of a J-aggregate increases relative to that of the monomer by a factor of $N_c$, from a comparison of lifetimes ($\tau_J$ vs $\tau_m$) and quantum yields ($\Phi_J$ vs $\Phi_m$), $N_c$ can be determined using the equation:

$$N_c = \frac{\tau_m \Phi_m}{\tau_J \Phi_J}$$

Figure 8. PM3-calculated models (a) top-down view of geometry-optimized macrocyclic structure, (b) molecular electrostatic potential map, (c) optimized structure tilted to emphasize steric crowding, (d) edge-on view of optimized structure, (e) frontier HOMO, (f) frontier LUMO, (g) edge-on view of the acyclic model structure, (h) and top-down view of the acyclic structure.
The data obtained suggest that $N_c$ is on the order of 12 for our 6a J-aggregate films. Coherent coupling also leads to a narrower total line width for the J-aggregate optical transition relative to the monomer because the delocalized exciton averages out site-to-site variations and suppresses the inhomogeneous broadening. The linewidths of the monomer optical transition and the J-band are dominated by inhomogeneous broadening. Nevertheless, the width of the J-band relative to the monomer spectrum does characterize the coherence of the system. The line width of the J-band is narrower than the monomer optical transition because in the J-aggregate state, the exciton is delocalized over the $N_c$ molecules that are coherently coupled, which tends to average out site-to-site inhomogeneities in the exciton energy. This motional narrowing is manifest in the smaller line width for J-aggregate absorption and emission spectra. This coherent coupling also results in the accelerated radiative process in the J-aggregate state, which translates into the higher observed QY and shorter exciton lifetime for the J-aggregate compared to the monomer.

Molecular Modeling. In order to better visualize the equilibrium geometry of the macrocycles 6a, 6b, and 12, molecular calculations were performed at the semiempirical PM3 level, using a model compound (Figure 8) with deliberately shortened alkyi side chains to enable more rapid completion of the calculation. As can be seen in Figure 8, the macrocycle is composed of two 1,3-butadiyne-linked planar dibenz[a,j]anthracene subunits that are slightly staggered relative to each other as a result of steric crowding in the middle of the molecule. Despite this structural distortion, the core of the macrocycle retains some overall planarity, which would still allow for intermolecular $\pi-\pi$ stacking interactions. By comparison, the acyclic analog shows greater nonplanarity (Figure 8g), since the two nonrestrained aromatic subunits have more freedom to minimize steric repulsions. As a result, $\pi-\pi$ stacking interactions in acyclic 15 may be weakened.

Conclusion

In summary, three dibenz[a,j]anthracene-based macrocycles have been synthesized and spectroscopically characterized. The conjugated macrocycles display pronounced photophysical properties in the solid state, such as the intense red-shifted absorbances, narrow linewidths, and small Stokes shifts, indicating J-aggregate formation. These new compounds may have the potential to be utilized in various optoelectronic devices (e.g., lasers, photovoltaics, and polaritonic devices).

Acknowledgment. This work was supported by the National Science Foundation and the Army Research Office’s IED Stand-Off Detection Research Program (W911NF-07-1-0654), and the U.S. Army through the Institute for Soldier Nanotechnologies (DAAD-19-02-0002).

Supporting Information Available: Full experimental details pertaining to the synthesis of all new compounds described herein. This material is available free of charge via the Internet at http://pubs.acs.org.

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