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Twofold C–H Activation Enables Synthesis of a Diazacoronenetype Fluorophore with Near Infrared Emission through Isosteric Replacement

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Abstract: The synthesis and photophysical properties of a soluble amide-embedded coronene is reported. The key step in this synthesis is the twofold C–H activation of diazaperylene by a rhodium(III)Cp* catalyst. This unprecedented structural motif shows intense fluorescence in the near infrared region with a small Stokes shift and a distinct vibronic structure, which exhibits a slight extent of negative solvatochromism. Comparison of this compound with some relevant compounds revealed the importance of the amide incorporation in the peripheral concave region including an angular position to retain high aromaticity reflecting that of parent coronene. Treatment of this compound with Lewis acid $B(C_6F_5)_3$ formed a bis-adduct, which exhibited enhanced aromaticity as a consequence of the increased double bond character of the amide C–N bonds.

Introduction

Organic chromophores with distinct photophysical properties are constantly used as fluorophores for various applications, such as organic light-emitting diodes (OLED), sensor technology, photosensitizers, and fluorescent probes for bioimaging.^[1] Besides chemical modification of known fluorophores by introducing additional substituents, the development of new structural motifs is a lasting challenge. One promising approach to this end is to dope polycyclic aromatic hydrocarbons (PAHs) with heteroatoms, such as B, N, P, and S atoms,^[2] or replace a part of their double bonds with isosteric bonds. For the latter strategy, a representative one is to introduce a C=N double bond, which endows the parent skeleton with an electron-accepting character (Figure 1a).^[3] Replacement with a B-N bond as an isostere of the C=C double bond has also attracted recent growing attention.^[4] Various intriguing B–N-containing PAHs have been produced,



Figure 1. (a) A replacement strategy with C=C isosteres for constructing a new PAH scaffold and chemical structures of amide-embedded PAHs and (b) relevant compounds 1-4 and a key precursor 5.

which can retain aromaticity in the PAH scaffolds dependent on the incorporation mode of the B–N bond. A crucial benefit to introduce these isosteric bonds is to enable reducing the symmetry of PAHs, perturb the electronic structure, and impart the skeleton with polarity. In general, PAHs with high symmetry tend to have their lowest-energy electronic transition with a forbidden character. In contrast, such replacement strategy would not only perturb the HOMO–LUMO energy gap, resulting in

bathochromic shifts of the absorption and emission maxima, but also alter the electronic transition with the allowed character, rendering it a promising approach to gain a new fluorophore motif.

Herein we focus our attention on employing an amide bond as an isosteric replacement of a C=C double bond (Figure 1a).[5-7] The amide C-N bond has a partial double bond character, which corresponds to one third of the π bond energy of the C=C bond, which should have a direct impact on the aromaticity of the PAH skeletons. Moreover, the amide carbonyl group would generate a local dipole to the skeleton and thereby give rise to the polaritydependent character of the absorption and fluorescent properties. There are two ways to introduce the amide bond into PAHs: either replacing the double bond at the outer K-region, or integration of the amide moiety to the peripheral concave region in a fashion that the inner angular carbon atom is replaced with the amide nitrogen atom with three distinct C-N bonds. The latter mode is particularly of interest because it would more significantly perturb the electronic structure and aromaticity by participation of the nitrogen lone pair to a hexagon aromatic ring.

The problem is the synthetic challenge of such structural motif. Recently, amide-embedded pyrene derivatives 1 have been synthesized by Gryko and coworkers^[6] and our group,^[7] independently (Figure 1b). In detail, we utilized a Co(III)Cp*catalyzed C-H activation and subsequent alkylation of 2phenylpyridines with diazo compounds followed by Lewis acidassisted nucleophilic annulation by the pyridyl nitrogen atom. Since then, related transformations to this structural motif have been developed using Co- or Rh-catalysis,^[8] as well as Pdcatalyzed carbonylation strategies.^[9] Previously, multi-step synthesis was required to access this motif.^[10] Transition metalcatalyzed C-H activation emerged as powerful tool for organic synthesis.^[11] Rhodium complexes have been utilized in various C-H activation reactions as efficient and unique catalysts.[12] While Rh(II)-catalyzed carbenoid insertion reactions into inert C-H bonds are well established,[13] the alkylation of C-H bonds through insertion of a rhodium carbene species into a rhodium(III)carbon bond is less explored.^[14] We envisioned that our synthetic strategy via C-H activation would allow us to access more expanded PAHs and, as an attractive candidate, we designed bis(amide)-embedded coronene 2.

Notably, amide-embedded pyrene 1 showed intriguing negative solvatochromism due to increased aromaticity with increasing the solvent polarity and, consequently, 1 behaves as "aza-pyrene" and exhibited blue-shifted absorption and emission bands in more polar solvents.^[6] Our interest in this study is to demonstrate the efficacy of this design strategy to produce amideembedded PAHs as "aza-PAH" analogues. Coronene, consisting of seven fused 6-membered rings, only shows the symmetryforbidden absorption band as the lowest-energy electronic transition around 425 nm.^[15] One example of diazacoronene 3 has been reported by Wang and coworkers, which exhibited the absorption (λ_{abs}) and emission (λ_{em}) maxima at 488 nm and 502 nm, respectively.^[16] In stark contrast, the synthesized diazacoronene analogue 2 exhibits pronouncedly red-shifted λ_{abs} and λ_{em} that reach the near infrared region with a high fluorescence quantum yield. Theoretical studies in comparison with some relevant molecules including its regioisomer 4 revealed that the position of the amide moieties plays a crucial role to gain these properties and 2 has a substantial contribution of a Clarsextet canonical structure (Figure 1). Moreover, the amide carbonyl groups provide an opportunity to tune the aromaticity and electronic structure by complexation with a Lewis acid, demonstrating an advantage of this design strategy in comparison with the conventional substitution with the C=N double bond. Herein we report these properties of **2** together with its X-ray crystal structures without and with $B(C_6F_5)_3$.

Results and Discussion

For the synthesis, we envisioned that the bis(amide)embedded coronene scaffold could be obtained by the twofold C-H activation of diazaperylene precursor 5 (Figure 1b), which was synthesized in four steps from commercially available compounds (Scheme 1).^[17] Thus, treatment of 1,5-diaminoanthraquinone 6 with a slight excess of sodium nitrite and sequential addition of potassium iodide resulted in the formation of 1,5diiodoanthraquinone 7. This reaction showed full conversion of 6. The relatively low yield was mainly due to the challenging purification of 7, which was poorly soluble in standard organic solvents. Treatment of 7 with copper(I) acetylide gave 1,5di(hexyn-1-yl)anthraquinone 8 in 82% yield with facile purification due to the increased solubility owing to the alkyl chains. Compound 8 was further transformed to dibutyl-substituted diazaperylene 5 in 91% yield by treatment with an excess amount of urea at high temperatures in DMF.



Scheme 1. Synthetic route to bis(amide)-embedded coronene **2**. For detailed conditions, see SI. TFE = 2,2,2-Trifluoroethanol. DMAP = 4-Dimethylaminopyridine.

For the final twofold C–H activation step, 2-diazo-4,4dimethyl-3-oxopentanoate was selected as a coupling partner, since the ester group was required for the C–N bond formation, while an additional electron-withdrawing keto group adjacent to the diazo group would stabilize the resulting carbene species. This stabilization effect is crucial for the reactivity as described previously.⁷ We also envisioned that the *tert*-butylcarbonyl group would help increasing the solubility of the target molecule **2**.

Treatment of **5** with 10 mol% of the cationic Rh(III)Cp* precursor [Rh(III)Cp*(MeCN)₃](SbF₆)₂ and a slight excess of the diazo compound in 2,2,2-trifluoroethanol (TFE) at 120 °C for 14 h, unfortunately, resulted in a mixture of the desired compound **2** and a mono-alkylated, mono-annulated product **9** due to insufficient nucleophilicity of the nitrogen atom at the electrophilic

carbon of the ester group. In the previous report,⁷ a Co(III)Cp* catalyst was used in order to facilitate the carbonyl activation due to its higher Lewis acidity. However, no conversion was observed for this transformation using the same Co(III)Cp* catalyst, likely due to the higher sensitivity of Co(III) to steric effects of the substrate. In contrast, it was found that simple addition of 10 mol% of 4-dimethylaminopyridine (DMAP) after 14 h to activate the ester group and additional heating of the reaction mixture resulted in the formation of the desired compound **2**, which was isolated in 15% yield as dark green crystals.

Compound 2 was unequivocally identified by NMR spectroscopy and mass spectrometry. Specifically, in the ¹H NMR spectrum in CD₂Cl₂, the compound showed three kinds of signals in the aromatic region, including the enamine C-H singlet peak at 7.91 ppm (Figure S12), indicative of retaining high aromaticity even for the amide-containing hexagon ring (vide infra). The structure of 2 was further identified by X-ray crystallographic analysis (Figure 2a). A single crystal suitable for the analysis was obtained by slow evaporation of a sample dissolved in a mixture of CH₂Cl₂/pentane (1:9, v/v).^[18] Compound 2 crystallized with one and a half molecules in the asymmetric unit. Both independent molecules present similar crystallographic bonds and angles parameters. Only one molecule (the entire molecule) is discussed below. The crystal structure showed that the *tert*-butylcarbonyl moiety has almost a perpendicular orientation against the polycyclic plane, which should be responsible for the high solubility. One of the amide-containing hexagon rings is slightly deviated from the plane of the polycyclic skeleton to avoid the steric congestion with the neighbouring exocyclic bonds. Notably, similar to the structure of parent coronene, the C-C bonds at the K-region tend to have shorter bond distances around 1.35-1.36 Å compared to those of the C–C bonds at the peripheral concave region (1.37–1.43 Å) (Figure 2b). The amide moiety also follows this trend that the amide C-N bond is rather long of 1.449(8) Å and 1.465(8) Å in contrast to the amide C-C(carbonyl) bond of 1.406(8) Å and 1.405(8) Å, while the carbonyl C=O bonds are subtly long of 1.236(7) Å and 1.235(7) Å. In the packing structure, the compound forms dimeric π -stacked motifs in an offset fashion with the short interplane distance of 3.32 Å (Figure S1).

The incorporation of the amide moiety into the PAH skeleton results in significant alternation of the electronic structure, which was proven by cyclic voltammetry (Figure 3). In CH₂Cl₂, compound **2** exhibited two reversible redox processes for reduction and one reversible redox process for oxidation. Notably, both of the two-electron reduction and one-electron oxidation processes were reversible for at least 10 cycles, indicating that the thus generated reduced and oxidized species are stable under the measurement conditions. The half wave potentials ($E_{1/2}$) in the reductive region were observed at less negative potential of -1.51 V and -1.92 V (vs Fc/Fc⁺), while the compound showed a rather less positive first oxidative potential of 0.31 V (vs Fc/Fc⁺), implying a narrow HOMO–LUMO gap. Reflecting this electronic characteristic, the compound exhibited both the absorption and emission in the near infrared (NIR) region (*vide infra*).





Figure 2. (a) Crystal structure of **2** (50% probability for thermal ellipsoids), where hydrogen atoms are omitted for clarity and (b) comparison in bond lengths [Å] between **2** (left) and coronene (right).^[19]



Figure 3. Cyclic voltammogram of bis(amide)-embedded coronene 2 in CH_2CI_2 : scan rate: 0.05 V s⁻¹; supporting electrolyte: [nBu_4N][PF₆] (0.1 M); all potentials referenced vs. Fc/Fc⁺.

In the absorption spectrum in CH₂Cl₂, compound 2 exhibited an intense band with a distinct vibronic structure in the NIR region (Figure 4). The spectral shape is in contrast to a broad and structureless absorption band of amide-embedded pyrene 1,[6,7] and more similar to those of coronene derivatives in terms of the distinct vibronic structure, except the forbidden character for the lowest-energy absorption band.^[15c] The molar absorption coefficient of 2 exceeds 5×10^4 M⁻¹ cm⁻¹, demonstrating the impact of the reduced symmetry by embedding the amide moieties. The absorption maximum (λ_{abs}) of **2** was significantly red-shifted to 673 nm, which is longer by 143 nm and 188 nm than those of **1** (R = C(O)OCH₃, λ_{abs} 530 nm)⁷ and diazacoronene **3** $(\lambda_{abs}$ 485 nm in CHCl₃),^[16] respectively. In fluorescence spectrum in the same solvent, bis(amide)-embedded coronene 2 showed a mirror-image emission band with a distinct vibronic structure. The emission maximum (λ_{em}) is 686 nm with a small Stokes shift of

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Figure 4. Absorption and emission spectra of 2 in CH₂Cl₂. Pictures show 2 in CH₂Cl₂ (C = 0.003 M) (left) and under UV irradiation (365 nm) (right).

282 cm⁻¹, which is much smaller than that of **1** (R = C(O)OCH₃, 1774 cm⁻¹).^[7] The fluorescence quantum yield of **2** was as high as 0.64 in CH₂Cl₂ and the full-width-at-half-maximum (FWHM) for the shorter-wavelength band was 29 nm. The fluorescence lifetime was determined by the time-resolved fluorescence spectra to be 13 ns, from which the radiative (k_r) and nonradiative (k_{nr}) decay rate constants from the singlet excited state were determined to be 4.9 × 10⁷ s⁻¹ and 2.8 × 10⁷ s⁻¹, respectively.

We also studied the solvent effect on the photophysical properties (Table S1). Going from nonpolar toluene to CH₂Cl₂, both the absorption and emission bands exhibited subtle blue shifts from 682 nm to 673 nm and from 692 nm to 686 nm for the λ_{abs} and λ_{em} , respectively. The fluorescence quantum yield is not significantly affected by the solvent polarity. The fact that the negative solvatochromism was observed even in the absorption spectra implies its less polar structure in a more polar solvent even in the ground state, although the extent of the blue shift is smaller than that of **1**.^[6]



Figure 5. TD-DFT calculation of 2' in toluene and CH_2Cl_2 calculated at the PBE0/6-31+G(d) level of theory and the pictorial drawings of Kohn-Sham HOMO and LUMO for 2' in CH_2Cl_2 .

To assign the electronic transition bands observed for 2, we conducted theoretical calculations for model compound 2' that furnishes ethyl groups instead of butyl groups. Time-dependent (TD) DFT calculation at the PBE0/6-31+G(d) level of theory gave

the electronic transition energies for the absorption consistent with the experimental results. The lowest-energy transition band is assigned to the π - π^* transition in which the HOMO-LUMO transition is dominant. Both the HOMO and LUMO are delocalized over the entire π skeleton including the amide moieties (Figure 5). Importantly, the oscillator strength for this transition is 0.347, demonstrating its symmetry-allowed character unlike parent coronene. Calculated optimized structures of 2' in the S₀ and S₁ (B3LYP/6-31+G(d) level of theory) suggested a small structural relaxation in the excited state with subtle bond-length changes. Franck-Condon analysis for the transition from the zero-point vibrational energy level in the S₁ to the S₀ was also conducted. The simulated fluorescence spectrum is well consistent with the experimental result. The vertical bending vibrational modes in the S₀ are relevant to the intense and small FWHM emission band at the shorter wavelength around 690 nm, while the stretching vibrational modes are involved in the second vibronic band at around 760 nm (Figures S6-8, Table S2).

The calculations including the solvent effect using the polarizable continuum model (PCM) reproduced the negative solvatochromism in the absorption spectra. Namely, the calculated absorption maximum was blue shifted from 624 nm (1.99 eV) in toluene to 614 nm (2.02 eV) in CH_2Cl_2 , whereas the HOMO and LUMO energy levels were essentially unchanged (Figure 5). Close inspection of the optimized structures in these solvents showed a slightly elongated amide C=O bond as well as a slightly shortened amide N–C bond (Figure S9), although the extent of the structural change is small, indicative of the increased aromaticity of the amide-embedded hexagon ring in a more polar solvent in the ground state.





To gain insight into the aromatic character of the amideembedded PAHs, the nucleus-independent chemical shift (NICS) calculations were conducted at the B3LYP/6-31+G(d) level of theory^[20] (Figure 6). The results showed that all hexagon rings A– F in the bis(amide)-embedded coronene **2'**, except the central ring G, retain high aromaticity in toluene with the NICS(1)_{zz} values in the range from –23.3 ppm to –16.2 ppm. This is in stark contrast to the aromatic character of the mono(amide)-embedded pyrene **1** (R = C(0)CH₃), in which the amide-embedded ring B only has the NICS(1)_{zz} value of –8.60 ppm, while those of the adjacent rings A and C are highly aromatic with the values of –31.6 ppm and –28.8 ppm, respectively. This significant difference between

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1 and 2' is rationalized by considering the aromatic character of the corresponding parent PAHs. In light of the Clar's rule, the rings A and C in pyrene have high aromaticity, while that of the ring B is moderate. In contrast, in coronene, the peripheral rings A retain high aromaticity, while the central ring B shows less aromaticity. The aromatic characters of the amide-embedded PAHs follow this trend and the rings B and E can retain high aromaticity despite the amide N-C bond in the hexagon ring. In other words, the amide substitution at the peripheral concave region can alter the electronic structure without significantly altering the aromatic character. This implication is worth noting when compared to the other substitution mode like in 4, where the amide-embedded ring B does not have high aromaticity by reflecting a dominant character of the perylene scaffold. The NICS calculation of 2' also showed that the increase in the solvent polarity from toluene to CH₂Cl₂ renders the NICS(1)_{zz} value of the ring B and E slightly more negative from -17.6 and -16.9 ppm to -18.0 and -17.2 ppm (Figure S10). This change is likely responsible for the experimentally observed negative solvatochromism.



Figure 7. (a) Absorption spectral change of $2~(1.17\times10^{-5}~M)$ in CH_2Cl_2 upon addition of $B(C_6F_5)_3$ and (b) crystal structure of $2[B(C_6F_5)_3]_2$ (50% probability of thermal ellipsoids), where hydrogen atoms and solvent molecules included in the crystalline lattice are omitted for clarity.

The amide-replacement strategy provides an additional option to modify the electronic structure of PAH, namely the complexation with a Lewis acid. Such electronic tuning has been

demonstrated for various *n*-conjugated systems containing Nheteroaryls or carbonyl groups, which generally results in decreasing their LUMO levels, and thereby gives rise to redshifted absorption and emission bands.[21] We envisioned that complexation of our amide-embedded coronene with a Lewis acid would enhance the double bond character of the amide C-N bonds and thereby increase the aromaticity of the amideembedded hexagon ring. Thus, we treated compound 2 with $B(C_6F_5)_3$ in CH_2CI_2 and monitored the change in the absorption spectra. Upon addition of $B(C_6F_5)_3$ to a solution of 2 (1.17 x 10⁻⁵ M), the intense sharp band for 2 at 673 nm gradually decreased in intensity and a new broad band appeared around 655 nm with a broad tail in the longer wavelength region. An isosbestic point was observed at 658 nm and 703 nm until addition of ca. 2.0 equiv of $B(C_6F_5)_3$, indicative of partial formation of a mono- $B(C_6F_5)_3$ adduct. Further increase in the amount of $B(C_6F_5)_3$ resulted in the rise of the broad absorption band with the λ_{abs} of 709 nm while decreasing the intensity of the absorption bands at 655 nm and 673 nm. We assumed the formation of bis-B(C₆F₅)₃ adduct $2[B(C_6F_5)_3]_2$, which was ultimately corroborated by the X-ray crystallographic analysis^[18] (vide infra). The resulting CH₂Cl₂ solution of $2[B(C_6F_5)_3]_2$ showed no fluorescence.

The crystal structure of $2[B(C_6F_5)_3]_2$ showed that two $B(C_6F_5)_3$ units sit above and below the plane of the amide-embedded coronene skeleton with the O–B distance of 1.571(6) Å. As a result of this complexation, the amide-embedded hexagon ring itself was deviated from the plane to a more extent compared to that of parent 2. Importantly, the amide N–C bond was shortened to be 1.418(6) Å, while the amide C–O bond length is elongated to 1.307(5) Å, indicative of the increased aromaticity by the complexation with $B(C_6F_5)_3$. Indeed, the NICS(1)_{zz} value of the amide-embedded ring, calculated using the crystal structure at the same level as that for 2', was more negative value of –21.4 ppm compared to those (–17.6 and –16.9 ppm) in 2' (Figure S11).

Conclusion

We succeeded in synthesizing bis(amide)-embedded coronene by the twofold C-H activation of a diazaperylene. The close inspection of its structure and properties in comparison with some relevant compounds revealed that the amide-replacement strategy is a useful design to alter the electronic structure of the PAH skeleton. The installation of the amide bond to the peripheral concave region is shown to be crucial for the retained high aromaticity of the parent skeleton. Therefore, the resulting compound behaves as a diaza-coronene (Figure 1). Notably, the synthesized bis(amide)-embedded coronene exhibited a far more significantly red-shifted absorption band compared to the known diazacoronene 3. Our diazacoronene has a deep green color and an intense NIR emission with the λ_{em} of 686 nm and a high fluorescence quantum yield of 0.64 in CH₂Cl₂. These properties demonstrate the efficacy of this design strategy to gain novel fluorophore skeletons for π -electron materials. An additional feature of this compound class is its capability to tune the electronic structure by the complexation with a Lewis acid. Taking advantage of a set of these properties we are currently working on expanding the application of this structural motif to various directions including bioimaging.

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Keywords: C–H activation • amide • coronene • fluorescence • aromaticity

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FULL PAPER

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Twofold C–H activation of diazaperylene by a rhodium catalyst produces a bis(amide)-embedded coronene, which retains high aromaticity and exhibits an intense near infrared fluorescence with a high quantum yield. Thus, the replacement of C=C double bonds with amides represents a useful strategy for emissive polycyclic aromatic hydrocarbons (PAH). Further complexation with $B(C_6F_5)_3$ enhances the aromaticity of the amide-embedded hexagon rings.

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