Self-Condensation of Pyrene-4,5-dione: An Approach To Generate **Functional Organic Fluorophores**

Farshid Shahrokhi[®] and Yuming Zhao*[®]

Department of Chemistry, Memorial University of Newfoundland, St. John's, NL A1B 3X7, Canada

Supporting Information

ABSTRACT: A new class of π -conjugated organic fluorophores containing a 6H-phenanthro[4,5-cde]pyreno[4',5':4,5]imidazo[1,2-a]azepin-6-one core was synthesized by a facile one-pot condensation method. The molecular structures and solid-state packing properties of these compounds were investigated by X-ray single crystallographic analysis. UV-vis absorption and fluorescence spectroscopic studies disclosed interesting mechanofluorochromic properties in the solid state and highly sensitive acidochromic behavior in the solution phase.



yrene derivatives are popular molecular building blocks in the development of advanced organic optoelectronic materials, owing to the rich electronic and photophysical properties of pyrene.¹ Studies in this area have been continuously motivated by the development of new functionalized pyrenes, which serve as useful precursors for the preparation of advanced π -conjugated materials.² In recent years, pyrene-4,5-dione³ has found growing application, especially after the disclosure of an efficient large-scale synthesis of pyrene-4,5-diones by Bodwell and co-workers.^{3c} Synthetically, pyrene-4,5-dione can undergo various reactions to yield more extended π -systems.⁴ Among them, condensation reactions constitute a very appealing approach due to their high efficiency and simplicity in operation.

In our recent study of pyrenoimidazole derivatives,^{4e} an interesting type of self-condensation reaction was discovered. As shown in Scheme 1, a mixture of pyrene-4,5-dione (1a),

Scheme 1. Synthesis of Pyrene Derivatives 2a-c through Self-Condensation of Pyrene-4,5-diones



ammonium acetate, and glacial acetic acid was heated at 100 °C for 10 h, resulting in the formation of 6H-phenanthro[4,5cde]pyreno[4',5':4,5]imidazo[1,2-a]azepin-6-one (2a) in 25% yield. Although 2a shows relatively low solubility in common organic solvents, its molecular structure could still be reasonably elucidated based on ¹H NMR and MS analyses (see the Supporting Information). To address the solubility problem, tbutyl substituted pyrene-4,5-diones 1b and 1c were prepared,^{3c} and they were subjected to the same self-condensation conditions to afford analogous products with both improved solubility and yields (Scheme 1). The molecular structures of condensation products 2b and 2c were unambiguously confirmed by X-ray single crystallography in addition to NMR and MS analysis. The X-ray structure of **2b** (Figure 1A) shows



Figure 1. ORTEP drawings (50% probability) of (A) 2b and (B) 2c as well as the packing motifs of their enantiomeric pairs in the crystalline state.

that the steric interactions between 6-one and pyrenyl 8-H make the molecule adopt a nonplanar helical shape. Two types of enantiomers with opposite helicity are observed in the crystal structure. As shown in Figure 1A, enantiomeric pairs of 2b are packed in a slip-stacked fashion. Density functional theory (DFT) calculations revealed that the racemization energy barriers of 2 are quite low (e.g., 6.46 kcal/mol for 2a, see Figure S-16, Supporting Information), suggesting that individual molecules of 2, in the gas phase or well dissolved in a solvent,

Received: September 19, 2019

Organic Letters

would undergo rapid configurational exchanges under standard conditions.

The molecular structure of 2c (Figure 1B) shows similarity to that of **2b**, but the π -stacking of each enantiomeric pair in the crystalline state appears to be more cofacial than 2b as a result of less *t*-butyl groups present in 2c. Note that 2-*t*-butylpyrene-4,5dione (1c) is an unsymmetrical diketone, which in theory may yield four different regioisomeric products through selfcondensation (see Figure S-17, Supporting Information). For example, Emery et al. reported that the self-condensation of an unsymmetric diketone under conditions similar to ours afforded two regioisomers in nearly equal yields.⁵ In our reaction. however, only one major product 2c was obtained from the selfcondensation of 1c. As DFT calculations indicated that the structure of **2c** is the least thermodynamically stable one among other possible self-condensation products (Figure S-17, Supporting Information), the regioselectivity of this reaction is likely kinetically controlled rather than thermodynamically controlled.

To gain a deeper insight into the reaction mechanism of the above self-condensation reactions, two control reactions were carried out. First, phenanthrene-9,10-dione (3) was subjected to heating in the presence of ammonium acetate and glacial acetic acid. This reaction only yielded phenanthroimidazole 4 as the major product (Scheme 2). Product 4 was formed as a

Scheme 2. Control Condensation Reactions of Phenanthrene-9,10-dione (3) and Pyrene-4,5-dione (1b)



precipitate with very poor solubility in common organic solvents due to the presence of a free carboxylic group. This outcome contrasts the cases of pyrene-4,5-diones but is consistent with the observation reported by Lantos in 1975.⁶ In another control reaction, a mixture of diones 1b and 3 was subjected to the same condensation conditions. In this reaction, two soluble products were isolated in nearly equal yields. The first product is 2b, resulting from the self-condensation of 1b. The second product turns out be a cross-condensation product 5 (Scheme 2). The molecular structure of 5 was validated by X-ray structural analysis (Figure 2A) in addition to NMR and MS. Similar to 2b/ c, enantiomeric pairs exist in the crystal structure of 5, and they form ordered columnar supramolecular assemblies through π stacking (Figure 2B). In theory, cross-condensation of two different diketones should yield two products. The fact that only 5 was formed suggests a high degree of regioselectivity, which deserves more light to be shed upon.

The two control reactions underscore the indispensable role of pyrene-4,5-dione in the formation of the seven-membered azepinone ring during the condensation process. Rationalization



Figure 2. (A) ORTEP drawing (50% probability) and (B) crystal packing diagram of compound 5. Hydrogen atoms are omitted for clarity.

for the different reactivities of pyrene-4,5-dione versus phenanthrene-9,10-dione can be made based on the reaction mechanisms outlined in Scheme 3. Herein, two reaction





pathways are illustrated for the self-condensation reactions of 3 and 1a, respectively. Phenanthrene-9,10-dione yields a diimine intermediate IM-1 when treated with ammonium acetate and glacial acetic acid. IM-1 then reacts with 3 through condensation to form a spiral intermediate IM-2, which undergoes a ring opening process through water nucleophilic attack to give product 4^{5-7} The rotational freedom at the biphenyl unit in 4 allows the carboxylic group to shun away from the imidazolyl group in order to minimize steric crowding. DFT optimized geometry of 4 shows that the distances between carboxylic carbon and two imidazolyl nitrogen atoms are 3.53 and 5.45 Å, respectively (Figure S-18, Supporting Information). Such a structure disfavors intramolecular condensation between the carboxylic and imidazolyl groups. Pyrene-4,5-dione 1a can also form a diimine intermediate IM-3, followed by a spiral intermediate IM-4. Ring opening of IM-4 leads to IM-5 in which the carboxylic group and the imidazolyl unit are closely positioned as a result of their direct linkage to the rigid phenanthrene unit. The distances between carboxylic carbon and two imidazolyl nitrogen atoms in the optimized geometry of IM-5 (Figure S-19, Supporting Information) are 3.03 and 3.08 Å, which are much shorter than those in 4. The preorganization of IM-5 thus enables the intramolecular condensation between the carboxylic and imidazolyl groups, which eventually yields 2a as a stable product.

Given the relatively good solubility of **2b** in organic solvents, it was further investigated by UV–vis absorption and fluorescence spectroscopic analysis to probe the electronic properties of these new pyrene-based π -systems. Figure 3A compares the UV–vis



Figure 3. (A) Normalized UV–vis absorption spectra of **2b** measured in different organic solvents. (B) Normalized fluorescence spectra of **2b** (in CCl₄) measured at different concentrations (λ_{ex} = 313 nm).

spectra of **2b** measured in different organic solvents. The absorption profiles of **2b** show similar features in most of the solvents examined, except in methanol and chloroform. In methanol, the lowest-energy $\pi \rightarrow \pi^*$ absorption band of **2b** is considerably blueshifted to 383 nm, while in chloroform it shows the most pronounced redshift ($\lambda_{max} = 400$ nm). The solvatochromic effects observed here do not follow a clear trend in correlation with solvent polarity. More likely, solubility and/ or aggregation effects play some critical roles in the electronic absorption properties of **2b**.

The emission properties of 2b in the solution phase were studied by fluorescence spectroscopy. Carbon tetrachloride was used as the solvent, considering the good solubility it affords. Figure 3B shows the fluorescence spectra of 2b measured at different concentrations. At relatively high concentration (10^{-4}) M), the spectrum features only one broad band peaking at 520 nm. When the concentration is reduced by 1 order of magnitude (10^{-5} M) , this emission band is slightly blueshifted to 505 nm. In the meantime, a new shoulder band emerges in the high-energy region (ca. 380-440 nm), and the relative intensity of this new band continues to increase under further diluted conditions (10^{-6} M) . The concentration-dependent fluorescence behavior can be attributed to the formation of excimers in solution.⁸ At high concentration, excimers dominate the emission process to give the long-wavelength band at 520 nm. At low concentration, however, the emission of individual molecules of 2b (i.e., monomers) becomes more significant in the range of 380-400 nm. As such, the fluorescence profile reflects the contributions of both excimers and monomers.

When 2b was dissolved in different organic solvents at concentration of 10^{-5} M, the solutions were found to emit different luminescent colors upon long-wavelength UV light irradiation (see Figure 4A). For solvents with good solubility, such as carbon tetrachloride, p-xylene, benzene, THF, and ethyl acetate, the solutions of 2b give greenish luminescence. For solvents with moderate solubility (chloroform, acetone, acetonitrile, and DMSO), the luminescent color is yellowish. For solvents with poor solubility such as methanol and ethanol, the luminescence is very weak. However, in hexane, the luminescent color is blue. The luminescent colors show a good correlation with the maximum emission wavelengths (λ_{em}) observed in their fluorescence spectra (Figure 4D). It was further noticed that compound 2b in the solid state exhibits mechanofluorochromic behavior. Crystals of 2b yield bluecolored luminescence. Subjecting the crystals to mechanical



Figure 4. (A) Photographic images of **2b** $(1.49 \times 10^{-5} \text{ M})$ dissolved or suspended in different organic solvents (λ_{em} values are indicated). (B) Photographic images of **2b** in crystalline form. (C) Photographic images of **2b** in powdery form. All samples were placed under the irradiation with a UV lamp (365 nm). (D) Fluorescence spectra of **2b** $(1.49 \times 10^{-5} \text{ M})$ measured in various solvents ($\lambda_{ex} = 313 \text{ nm}$). (E) Normalized fluorescence spectra of **2b** measured in crystalline and powdery forms ($\lambda_{ex} = 350 \text{ nm}$).

grinding resulted in amorphous powder, which gave greencolored luminescence (Figure 4B,C). Solid-state fluorescence spectroscopic analysis showed that crystals of 2b emit a broad peak around 508 nm, while the powder of **2b** (amorphous state) yields two emission bands at 441 and 508 nm, respectively (Figure 4E). The mechanofluorochromic properties of **2b** can be attributed to the emission of excimers and monomers. In crystalline state, 2b molecules are closely stacked to facilitate the formation of excimers when they are electronically excited. As such, the emission profile of 2b only features the longwavelength excimer band, which yields blue-colored luminescent light. In amorphous solid state, 2b molecules are randomly and disorderly packed, so they emit both long-wavelength (excimer) and short-wavelength (monomer) light. The combined emission bands thus constitute the observed greencolored luminescence.

The solutions of **2b** were also found to show acidochromic fluorescence behavior. As shown in Figure 5, the fluorescence intensity of **2b** grows steadily with increasing addition of a strong organic acid, trifluoroacetic acid (TFA). The fluorescence enhancement reached saturation after ca. 3100 mol equiv of TFA was added, while the λ_{em} was observed to redshift in a



Figure 5. Fluorescence spectra of **2b** $(1.49 \times 10^{-4} \text{ M in CCl}_4)$ in response to the addition of TFA from 0 to 3.10×10^3 molar equivalents. (B) Plot of maximum emission intensity against equivalents of TFA.

moderate degree, from 513 to 530 nm, during the TFA titration. The relative fluorescence quantum yield ($\phi_{\rm F}$) of **2b** was determined to be 0.101 in CCl₄, and it was increased to 0.340 after addition of excess TFA (3100 equiv).

To understand the detailed interacting modes between **2b** and TFA in the solution phase, ¹H NMR titration experiments were performed, and the results are given in Figure 6. The aromatic



Figure 6. ¹H NMR spectra of 2b $(6.41 \times 10^{-3} \text{ M in } \text{CD}_2\text{Cl}_2)$ in response to the addition of TFA from 0 to 9.21 mol equiv. Signals of protons at 15 and 17 positions are highlighted.

proton signals exhibit varied degrees of shift with TFA addition, while the most significant changes can be noted in the downfield region of the spectrum. Herein, the two doublets at 9.63 and 9.17 ppm are assigned to the aromatic protons at 17 and 15 positions (referred to as H₁₇ and H₁₅) according to DFT calculations (Figure S-21, Supporting Information). Upon addition of TFA, the imidazolyl nitrogen atom (N_{16}) is protonated since it is the most basic site in the molecule. The proposed protonation mode is also corroborated by the singlecrystal structure of the complex of $[2b \cdot (TFA)_2]$ (shown in Figure S-23A, Supporting Information). Eventually, the protonation of 2b with TFA leads to a substantial degree of upfield shift of H_{17} (from 9.63 to 8.95 ppm), while the signal of H_{15} is only moderately shifted from 9.17 to 9.06 ppm. In the crystal structure of protonated 2b, the newly formed imidazolium N-H group shows a much closer distance to H₁₇ than to H_{15} . This accounts for that observation that the H_{17} signal is the most shifted after protonation. The X-ray packing diagram (Figure S-23B, Supporting Information) indicates that complexation of 2b with TFA leads to highly ordered supramolecular assemblies. It is therefore reasonable to propose that addition of TFA to the solution of 2b could also enhance intermolecular interactions, which facilitate excimer formation and increase fluorescence emission.

In summary, we have discovered a straightforward synthetic method to construct polycyclic aromatic structures based on 6*H*-phenanthro[4,5-*cde*]pyreno[4',5':4,5]imidazo[1,2-*a*]-azepin-6-one. Interesting solvatofluorochromic, mechanofluor-

ochromic, and acidochromic fluorescence properties were observed for this new class of pyrene-based organic fluorophores, and the origins of these fluorescence behaviors can be attributed to excimer/monomer equilibria. Our findings open a new avenue for the development of pyrene-based luminescent materials with potential applications in advanced molecular optoelectronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03297.

Detailed experimental procedures, characterization, and DFT calculation results (PDF)

Accession Codes

CCDC 1946909–1946911 and 1952458 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yuming@mun.ca.

ORCID 💿

Farshid Shahrokhi: 0000-0001-8222-5817 Yuming Zhao: 0000-0002-1300-9309

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank NSERC and Memorial University for funding support. Dr. Michael Ferguson at University of Alberta and Dr. Michael Katz at Memorial University are acknowledged for assistance in the X-ray single crystallographic analysis.

REFERENCES

(1) (a) Figueira-Duarte, T. M.; Müllen, K. Pyrene-based materials for organic electronics. *Chem. Rev.* **2011**, *111*, 7260–7314. (b) Li, J.; Chen, S.; Wang, Z.; Zhang, Q. Pyrene-fused acenes and azaacenes: synthesis and applications. *Chem. Rec.* **2016**, *16*, 1518–1530.

(2) (a) Mateo-Alonso, A. Pyrene-fused pyrazaacenes: from small molecules to nanoribbons. *Chem. Soc. Rev.* 2014, 43, 6311-6324.
(b) Casas-Solvas, J. M.; Howgego, J. D.; Davis, A. P. Synthesis of substituted pyrenes by indirect methods. *Org. Biomol. Chem.* 2014, 12, 212-232. (c) Zöphel, L.; Enkelmann, V.; Rieger, R.; Müllen, K. Saddle shaped hexaaryl[*a,c,fg,j,l,op*]tetracenes from 4,5,9,10-tetrafunctionalized pyrenes. *Org. Lett.* 2011, 13, 4506-4509. (d) Feng, X.; Hu, J. Y.; Redshaw, C.; Yamato, T. Functionalization of pyrene to prepare luminescent materials-typical examples of synthetic methodology. *Chem. - Eur. J.* 2016, 22, 11898-11916.

(3) (a) Young, E. R.; Funk, R. L. A practical synthesis of pyrene-4, 5dione. J. Org. Chem. **1998**, 63, 9995–9996. (b) Hu, J.; Zhang, D.; Harris, F. W. Ruthenium(III) chloride catalyzed oxidation of pyrene and 2,7-disubstitued pyrenes: an efficient, one-step synthesis of pyrene-4,5-diones and pyrene-4,5,9,10-tetraones. J. Org. Chem. **2005**, 70, 707– 708. (c) Walsh, J. C.; Williams, K. L. M.; Lungerich, D.; Bodwell, G. J. Synthesis of pyrene-4,5-dione on a 15 g scale. *Eur. J. Org. Chem.* **2016**, 2016, 5933–5936.

(4) (a) Prakash Rao, H. S.; Vijjapu, S. Synthesis and photochromic properties of benzofuran-phenanthrene and benzofuran-pyrene

hybrids. RSC Adv. 2014, 4, 25747-25758. (b) Fan, Q.; Liu, Y.; Xiao, M.; Tan, H.; Wang, Y.; Su, W.; Yu, D.; Yang, R.; Zhu, W. Donoracceptor copolymers based on benzo[1,2-b:4,5-b']dithiophene and pyrene-fused phenazine for high-performance polymer solar cells. Org. Electron. 2014, 15, 3375-3383. (c) Gu, P.-Y.; Zhang, J.; Long, G.; Wang, Z.; Zhang, Q. Solution-processable thiadiazoloquinoxalinebased donor-acceptor small molecules for thin-film transistors. J. Mater. Chem. C 2016, 4, 3809-3814. (d) Liu, Y.; Bai, Q.; Li, J.; Zhang, S.; Zhang, C.; Lu, F.; Yang, B.; Lu, P. Efficient pyrene-imidazole derivatives for organic light-emitting diodes. RSC Adv. 2016, 6, 17239-17245. (e) Tabasi, Z. A.; Younes, E. A.; Walsh, J. C.; Thompson, D. W.; Bodwell, G. J.; Zhao, Y. Pyrenoimidazolyl-benzaldehyde fluorophores: synthesis, properties, and sensing function for fluoride anions. ACS Omega 2018, 3, 16387-16397. (f) Karthik, S.; Ajantha, J.; Nagaraja, C.; Easwaramoorthi, S.; Gandhi, T. Synthesis and photophysics of extended π -conjugated systems of substituted 10-aryl-pyrenoimidazoles. Org. Biomol. Chem. 2016, 14, 10255-10266. (g) Mardanya, S.; Karmakar, S.; Mondal, D.; Baitalik, S. An imidazolyl-pyreno-imidazole conjugate as a cyanide sensor and a set-reset memorized sequential logic device. Dalton Trans. 2015, 44, 15994-16012. (h) Jadhav, T.; Dhokale, B.; Mobin, S. M.; Misra, R. Aggregation induced emission and mechanochromism in pyrenoimidazoles. J. Mater. Chem. C 2015, 3, 9981-9988.

(5) Emery, F. S.; Maria do Carmo, F.; de Simone, C. A.; Malta, V. R.; da Silva Júnior, E. N.; Pinto, A. V. Complex diazaazulenones from the reaction of *ortho*-naphthoquinones with ammonium acetate. *Synlett* **2010**, 2010, 1931–1934.

(6) Lantos, I. Reaction of phenanthrenequinone with ammonium acetate. J. Org. Chem. 1975, 40, 1641–1642.

(7) Biegger, P.; Schaffroth, M.; Brödner, K.; Tverskoy, O.; Rominger, F.; Bunz, U. H. Bisalkynylated 3,6-diiminocyclohexa-1,4-diene-1,4-diamine. *Chem. Commun.* **2015**, *51*, 14844–14847.

(8) (a) Förster, T. Excimers. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 333–343. (b) Winnik, F. M. Photophysics of preassociated pyrenes in aqueous polymer solutions and in other organized media. *Chem. Rev.* **1993**, 93, 587–614.