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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF 1,6-METHANO-[10]ANNULENE-FUSED AND 2,4-DIMETHYL-7,12-METHANO-3H-CYCLOHEPTA[10]ANNULEN-3-ONE-FUSED 10H-PYRROLO[1,2-*a*]-PERIMIDIN-10-ONES

Shigeyasu Kuroda,^{a,*} Naoko Matsumoto,^a Yanmei Zhang,^a Takako Abe,^a Yoshikazu Horino,^a Yurie Fujiwara,^b and Mitsunori Oda^{b,*}

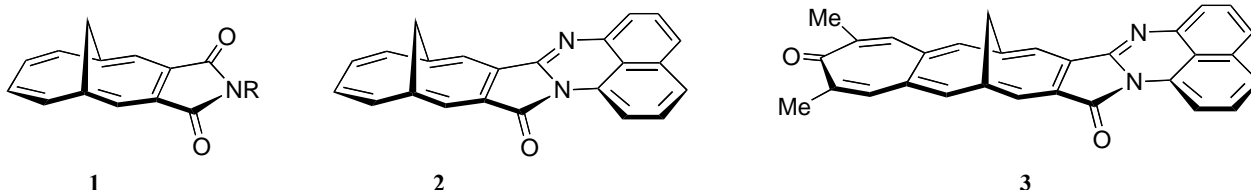
^aGraduate School of Science and Engineering, Faculty of Nano and Functional Materials Science, University of Toyama, Gofuku 3190, Toyama, 930-8555 Japan,

^bDepartment of Chemistry, Faculty of Science, Shinshu University, Asahi 3-1-1, Matsumoto, Nagano, 390-8621 Japan, e-mail: kuro@eng.u-toyama.ac.jp

Abstract – The title 1,6-methano[10]annulene-fused and 2,4-dimethyl-7,12-methano-3H-cyclohepta[10]annulen-3-one-fused 10H-pyrrolo[1,2-*a*]perimidin-10-ones, denoted by **2** and **3**, respectively, were synthesized. A novel and efficient synthetic method involving tandem [4 + 3] cycloaddition and 10 π -electrocyclization was developed for constructing the 2,4-dimethyl-7,12-methano-3H-cyclohepta[10]annulen-3-one skeleton toward the synthesis of **3** from 6H-cyclohepta[*c*]furan-5,7-dicarbaldehyde (**5**). Spectroscopic properties of **2** and **3** were also described in relation to the tropone-fusion.

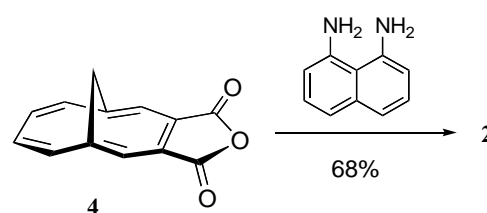
This paper is dedicated to Dr. Albert Padwa on the occasion of his 75th birthday

Recently, Zuo *et al.* and we reported the synthesis of 1,6-methano[10]annulene-3,4-dicarboximides (**1**).^{1,2} We also disclosed that most imides having the general structure **1** exhibited the emission of green light in a narrow range of 467–472 nm upon excitation and that their emission quantum yields depended on the substituent on the nitrogen atom.² In order to develop materials having a 1,6-methano[10]annulene-3,4-

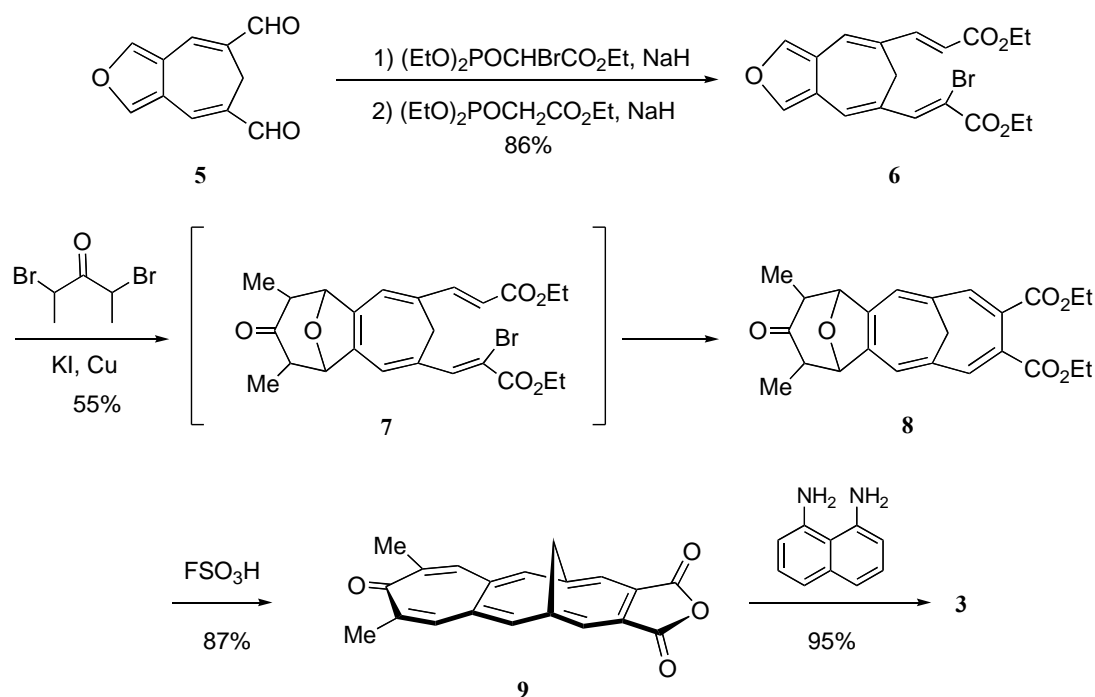


dicarboximide skeleton with emission of longer wavelength light, we have been interested in π -extended derivatives of **1**, namely 1,6-methano[10]-annulene-fused and 2,4-dimethyl-7,12-methano-3*H*-cyclohepta[10]annulen-3-one-fused 10*H*-pyrrolo[1,2-*a*]perimidin-10-ones, **2** and **3**.³ In this communication, we describe the synthesis and spectroscopic properties of **2** and **3**. Furthermore, this study highlights the development of a novel synthetic method for constructing the 2,4-dimethyl-7,12-methano-3*H*-cyclohepta[10]annulen-3-one-fused 1,6-methano[10]annulene skeleton toward the synthesis of **3**.

The synthesis of **2** was achieved by condensation of 1,6-methano[10]annulene-3,4-dicarboxylic anhydride (**4**)^{1,2} with 1,6-diaminonaphthalene as shown in Scheme 1. Compound **2** was obtained as red microcrystals in 68% yield.⁴ On the other hand, the synthesis of **3** was accomplished in six steps starting from 6*H*-cyclohepta[*c*]furan-5,7-dicarbaldehyde (**5**)⁵ as shown in



Scheme 1. Synthesis of **2** from **4**



Scheme 2. Synthesis of **3** from **5**

Scheme 2. Consecutive Horner–Wadsworth–Emmons olefinations of **5** gave **6** in an overall yield of 86%. The treatment of **6** with 2,4-dibromo-3-pentanone in the presence of KI/Cu in refluxing acetonitrile gave **8**⁶ in 55% yield. This conversion involved a [4 + 3] cycloaddition⁷ at the furan ring of **6**, forming the tetrahydroheptalenone skeleton of intermediate **7**, followed by a thermal 10 π -electrocyclization and subsequent debromination of **7**, leading to the formation of the methano[10]annulene core. Treatment of **8** with fluorosulfonic acid facilitated not only the dehydration of the ether linkage in the

seven-membered ring of **8** but also concomitant formation of an anhydride group to give **9** in 87% yield. Finally, condensation of **9** with 1,6-diaminonaphthalene in refluxing DMF afforded **3** as deep red microcrystals in 95% yield. It should be noted that the series of reactions in Scheme 2 represents a novel and efficient method for constructing a tropone-fused 1,6-methano[10]annulene framework. Although we had already reported the synthesis of 3,4-tropono-1,6-methano[10]annulene,⁸ the method developed in this study provides an efficient alternative route to this ring system. Since a furan ring can be transformed into various functional groups, such as dialdehydes, lactones, and acetals, the utility of this method could be extended to the synthesis of 3,4,8,9-functionalized 1,6-methano[10]annulenes.

The UV–vis absorption and emission spectra of **2** and **3** are shown in Figures 1 and 2, respectively. The UV-vis absorption spectra in CH₂Cl₂ show main absorption maxima at 291 and 486 nm for **2** and at 334 and 494 nm for **3**. The shorter wavelength bands of **2** and **3** exhibit relatively large intensities and a large difference of 42 nm, while the longer wavelength bands exhibit small intensities and a modest difference of only 8 nm, suggesting that the latter bands are derived from excitation of the common chromophore, the pyrrolo[1,2-*a*]perimidin-10-one fragment, in **2** and **3**. In other words, the fused tropone does not have a significant effect on the shift of the long wavelength absorption. Compound **2** exhibits emission at 456

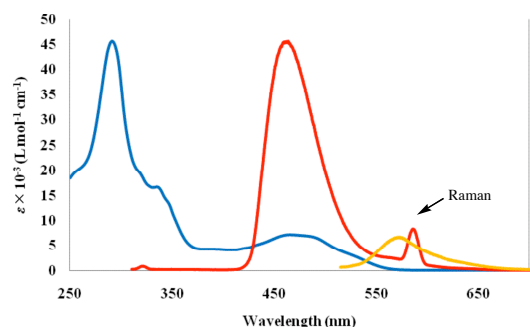


Figure 1. Absorption and emission spectra of **2** in CH₂Cl₂; The absorption spectrum by a blue line, the normalized emission spectrum upon excitation at 291 nm by a red line, the normalized emission spectrum upon excitation at 486 nm by an orange line

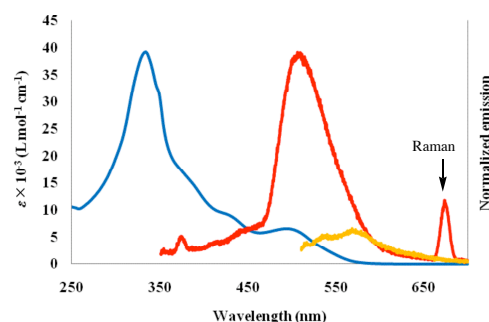


Figure 2. Absorption and emission spectra of **3** in CH₂Cl₂; The absorption spectrum by a blue line, the normalized emission spectrum upon excitation at 334 nm by a red line, the normalized emission spectrum upon excitation at 494 nm by an orange line

and 561 nm upon excitations at 291 and 486 nm, respectively. Interestingly, these two emission peaks are observed upon excitations at 322 nm at a time (*vide infra*). Following excitations at 334 and 494 nm, compound **3** exhibits emission at 501 and 561 nm, respectively. The emission curve resulting from excitation at 334 nm additionally includes the 561 nm peak at its foot slope. These emission behaviors of **2** and **3** are in contrast to those of **1**, which emit light only from the lowest excited state. Emission quantum yields upon excitation at 356 nm were determined to be 4.8×10^{-3} for **2** and 1.1×10^{-4} for **3**, which are far smaller than those of **1**.⁹ In acidic media, UV-vis absorptions of **2** and **3** vary. In a solution of 1% CF₃CO₂H in CH₂Cl₂, **2** and **3** show three and two distinct absorption bands in the range 250–400 nm, respectively, and their long wavelength absorptions appear as broad bands (Figures 3 and 4).

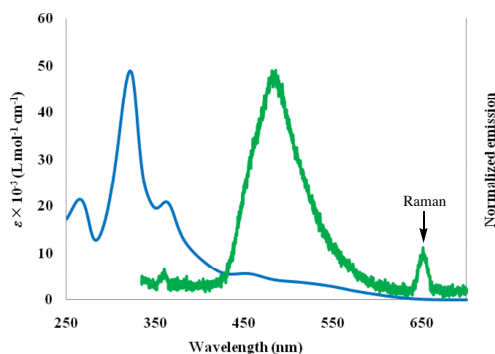


Figure 3. Absorption (blue) and normalized emission (green) spectra of **2** in 1% CF₃CO₂H-CH₂Cl₂. The emission spectrum was recorded upon excitation at 322 nm

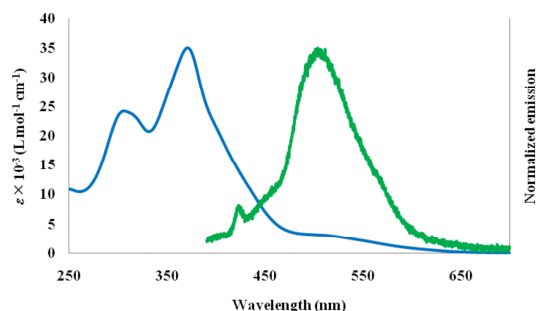


Figure 4. Absorption (blue) and normalized emission (green) spectra of **3** in 1% CF₃CO₂H-CH₂Cl₂. The emission spectrum was recorded upon excitation at 372 nm

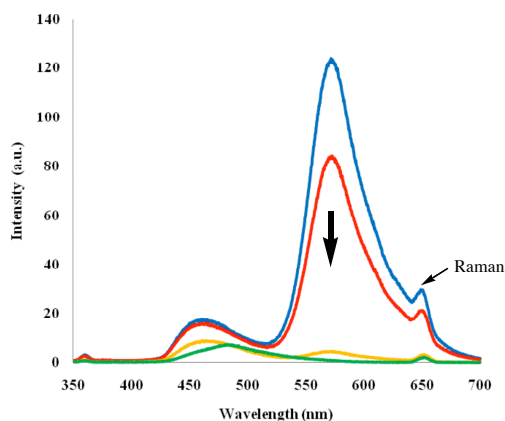


Figure 5. Emission spectra of **2** upon excitation at 322 nm in CH₂Cl₂ (blue line), 0.01% CF₃CO₂H-CH₂Cl₂ (red line), 0.1% CF₃CO₂H-CH₂Cl₂ (yellow line), and 1% CF₃CO₂H-CH₂Cl₂ (green line)

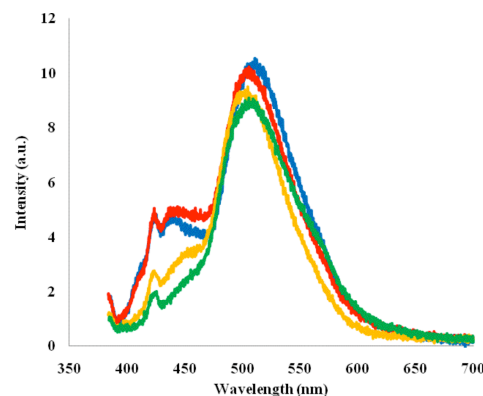


Figure 6. Emission spectra of **3** upon excitation at 372 nm in CH₂Cl₂ (blue line), 0.01% CF₃CO₂H-CH₂Cl₂ (red line), 0.1% CF₃CO₂H-CH₂Cl₂ (yellow line), and 1% CF₃CO₂H-CH₂Cl₂ (green line)

Emissions of **2** and **3** in this solvent system also vary. Compound **2** exhibits emission at 480 nm upon excitation at 322 nm and **3** emits at 496 nm upon excitation at 372 nm. It is noteworthy that the emission of **2** changes dramatically depending on the concentration of CF₃CO₂H in CH₂Cl₂,¹⁰ while the emission of **3** does not (Figures 5 and 6). This suggests that compound **2** can be used for sensing an acid in an organic solvent by monitoring its emission spectrum, though it is not yet clear why such a drastic quenching of the emission of **2** occurs by simply adjusting the pH. Further structural modifications to **2** and analyses of the spectroscopic properties of the resulting analogs are currently in progress.

In conclusion, we have synthesized the title 10*H*-pyrrolo[1,2-*a*]perimidin-10-one derivatives, **2** and **3**. For the synthesis of **3**, we have developed a novel and efficient synthetic method involving tandem [4 + 3] cycloaddition and 10π-electrocyclization reactions for construction of the tropono-1,6-methano[10]annulene skeleton from 6*H*-cyclohepta[*c*]furan-5,7-dicarbaldehyde (**5**). The absorption and

emission properties of **2** and **3** were also studied to evaluate the effects of the fused tropone. Incorporation of this fused ring onto **2** brought about restraint in quenching of the emission by protonation, and also resulted in a reduction in quantum yield.

ACKNOWLEDGEMENTS

We thank Ms Naoko Tamura at the University of Toyama for her preliminary research assistance in the preparation of compound **3**.

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2. S. Kuroda, N. Tamura, R. Miyatake, N. Matsumoto, Y. Horino, D. Miyawaki, and M. Oda, [Heterocycles](#), 2011, **83**, 789.
3. For most recent photophysical properties of the pyrroperimidinone derivatives, see; S. Goswami, D. Sen, N. K. Das, and G. Hazra, [Tetrahedron Lett.](#), 2010, **51**, 5563.
4. Selected physical properties of new compounds are as follows. **2**: Mp 242-244 °C; IR (KBr) ν_{\max} = 3033w, 2946w, 1706vs, 1634vs, 1582s, 1498m, 1407s, 1379m, 1328m, 1195m, 1159m, 1104m, 882w, 824m, 767m, 732m, 608w, 574w cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 8.54 (s, 1H), 8.51 (dd, J = 7.9, 1.6 Hz, 1H), 8.34 (s, 1H), 7.71 (m, 2H), 7.524 (dd, J = 7.9, 1.6 Hz, 1H), 7.520 (dd, J = 7.9, 1.6 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 7.46 (t, J = 7.9 Hz, 1H), 7.41 (dd, J = 7.9, 1.2 Hz, 1H), 7.33 (m, 2H), -0.08 (dt, J = 9.6, 1.2 Hz, 1H), -0.13 (dt, J = 9.6, 1.2 Hz, 1H) ppm; UV-vis (CH_2Cl_2) λ_{\max} = 291 (log ϵ = 4.66), 320sh (4.28), 335 (4.22), 347sh (4.13), 465 (3.85), 486 (3.83) nm; MS m/z (rel int) 334 (M^+ , 100), 333 ($\text{M}^+ - 1$, 7), 305 (36), 277 (3), 167 (4), 153 (9), 127 (5). HRMS m/z Calcd for $\text{C}_{23}\text{H}_{14}\text{N}_2\text{O}$ (M^+) 334.1106, found 334.1096. **3**: Mp 279-281 °C. IR (ATR) ν_{\max} = 2925w, 1700s, 1634s, 1588s, 1498w, 1455m, 1406s, 1372m, 1331w, 1198m, 1157s, 1100m, 915s, 825s, 759s, 717s cm^{-1} ; ^1H -NMR (CDCl_3 , 400 MHz) δ = 8.63 (s, 1H), 8.49 (dd, J = 7.9, 1.2 Hz, 1H), 8.47 (s, 1H), 7.75 (s, 2H), 7.67 (s, 1H), 7.65 (s, 1H), 7.53 (dd, J = 7.9, 1.2 Hz, 1H), 7.51 (dd, J = 7.9, 1.2 Hz, 1H), 7.459 (t, J = 7.9 Hz, 1H), 7.453 (t, J = 7.9 Hz, 1H), 7.36 (dd, J = 7.9, 1.2 Hz, 1H), 2.39 (s, 6H), 0.74 (dt, J = 9.6, 1.2 Hz, 1H), -0.27 (dt, J = 9.6, 1.2 Hz, 1H) ppm; UV-vis (CH_2Cl_2) λ_{\max} = 334 (log ϵ = 4.59), 348sh (4.51), 387sh (4.17), 431sh (3.95), 494 (3.82) nm; MS m/z (rel int) 440 (M^+ , 26%), 412 (47), 216 (28), 97 (39), 55 (100). HRMS m/z Calcd for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_2$ (M^+) 440.1525, found 440.1525. **6**: a slightly yellow oil; ^1H -NMR (CDCl_3 , 400 MHz) δ = 7.80 (s, 1H), 7.58 (s, 2H), 7.42 (d, J = 16.0 Hz, 1H), 7.20 (s, 1H), 6.83 (s, 1H), 6.09 (d, J = 16.0 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 4.24 (q, J = 7.2 Hz, 2H), 3.36 (s, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H) ppm. **8**: a yellow oil; ^1H -

NMR (CDCl₃, 400 MHz) of the major stereoisomer, δ = 7.89 (s, 2H), 7.41 (s, 2H), 5.15 (d, J = 5.0 Hz, 2H), 4.36 (q, J = 7.0 Hz, 4H), 3.17 (qd, J = 7.6, 5.0 Hz, 2H), 1.38 (t, J = 7.0 Hz, 6H), 1.09 (d, J = 7.6 Hz, 6H), -0.22 (d, J = 9.6 Hz, 1H), -0.27 (d, J = 9.6 Hz, 1H) ppm; ¹H-NMR (CDCl₃, 400 MHz) of the minor stereoisomer, δ = 7.82 (s, 2H), 7.31 (s, 2H), 5.35 (d, J = 5.0 Hz, 2H), 4.19 (q, J = 7.0 Hz, 4H), 2.97 (qd, J = 7.1, 5.0 Hz, 2H), 1.26 (t, J = 7.0 Hz, 6H), 1.04 (d, J = 7.1 Hz, 6H), 0.04 (d, J = 9.6 Hz, 1H), -0.12 (d, J = 9.6 Hz, 1H) ppm. **9**: yellow microcrystals, Mp >250 °C (dec.); ¹H-NMR (CDCl₃, 400 MHz) δ = 8.52 (s, 2H), 7.70 (s, 2H), 7.61 (s, 2H), 2.39 (s, 6H), 0.74 (d, J = 9.2 Hz, 1H), -0.16 (d, J = 9.2 Hz, 1H) ppm. Assignment of the proton signals of **2** and **3**, based on homodecoupling and NOE experiments, are as shown in Figure 7.

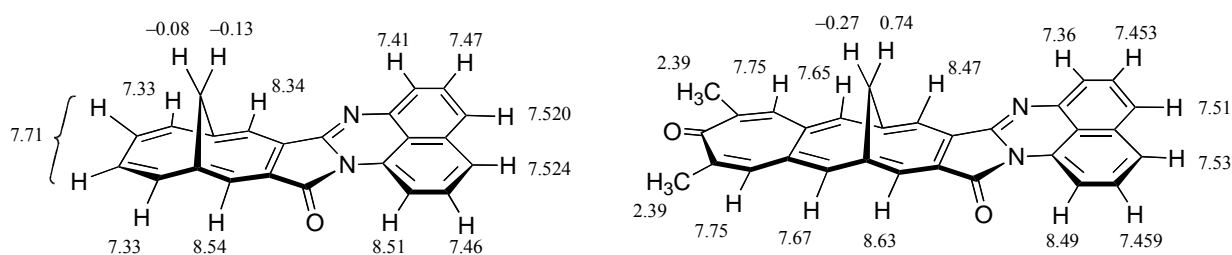


Figure 7. Assignment of proton signals for **2** (left) and **3** (right).

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- Compound **8** was obtained as an inseparable mixture of two stereoisomers. Signals for the two methyl groups on the seven-membered ring and the two ethyl groups of the esters appear to be equivalent for both stereoisomers in the ¹H NMR spectrum, suggesting that these isomers have σ -symmetry through a plane containing both the carbon and hydrogen atoms of the methano bridge. Since both isomers have coupling constants of 5 Hz between adjacent methine protons on the seven-membered ring, relative stereochemistry between the methyl groups and the ether group is assigned as trans for both isomers, based on previously analyzed NMR data by Hoffmann *et al.* However, the stereochemical relationship between the ether and methano bridges has been obscure. H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Am. Chem. Soc.*, 1972, **94**, 3940.
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- Emission quantum yields were determined by comparison of the total emission area with that of

anthracene ($\Phi = 0.27$, upon excitation at 356 nm in ethanol). Corrections were made based on the refractive indices for the different solvents, $n = 1.37$ (ethanol) and $n = 1.42$ (dichloromethane). The small quantum yields of **2** and **3** may be attributed to the low-lying $n-\pi^*$ excited state.

10. For emission quenching of a 10*H*-pyrrolo[1,2-*a*]perimidin-10-one derivative with Cu(II) ion, see ref 3. For tuning the photoluminescent wavelength of a pyridine-capped oligothiophene by proton bonding, see; M. Kondo, J. Miyake, K. Tada, and N. Kawatsuki, [Chem. Lett., 2011, 40, 264](#).