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# SYNTHESIS AND PHOTOPHYSICAL PROPERTY OF METHANOBENZO[10]ANNULENE-2,3:8,9-BIS(DICARBOXIMIDE) DERIVATIVES

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**Abstract** – Bis(dicarboximide) derivatives possessing methanobenzo[10]annulene skeleton were synthesized. The annulation of another dicarboximide on mono(dicarboximide), namely 1,6-methanobenzo[10]annulene-3,4-dicarboximide, provided the improvement of their molar extinction coefficients and fluorescence quantum yields. The change in photophysical behavior between mono(dicarboximide) and bis(dicarboximide) was explained by collaboration with theoretical calculations.

2,3-Naphthalimides **1** and 2,3-anthraimides **2** have attracted much attention due to their photophysical behavior and application to fluorescent probes. As examples, Heagy *et al*. reported the applications of dual fluorescent *N*-aryl-2,3-naphthalimide **1'** for DNA probe,[1] and Ohrui, Akasaka, and their colleagues developed a chiral 2,3-anthraimide **2'** as a chromophore.[2] The π-electronically analogy between 1,6-methano[10]annulene, whose annulene ring is crosslinking by one carbon atom, and naphthalene is expected to prosper the dicarboximide system. In addition, 1,6-methano[10]annulene can obtain the higher energy level of HOMO compared to the naphthalene due to the small aromatic stabilization energy,[3] and its increased solubility will also be useful. With this background in mind, 1,6-methanobenzo[10]annulene fused dicarboximides **3** have been studied so far (Figure 1b).[4]

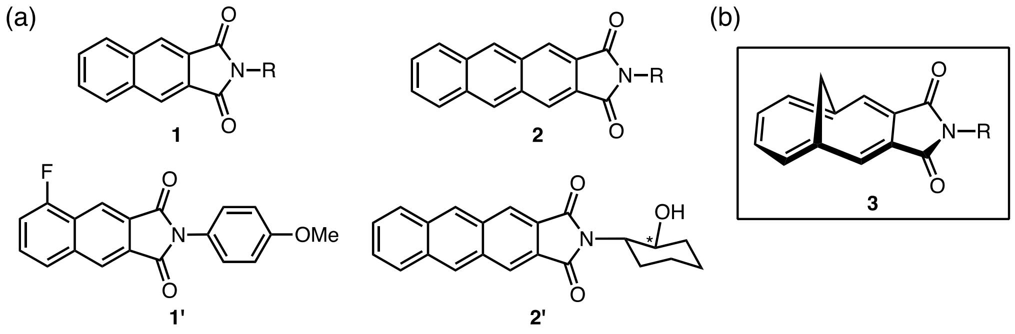


**Figure 1.** (a) 2,3-Naphthalimides **1**, 2,3-anthraimides **2**, and their applications **1'**, **2'**, (b) 1,6-Methano[10]annulene-3,4-dicarboximides **3**

Recently, we have found the one-pot synthesis of 1,6-methano[10]annulene-3,4-dicarboximides **3**, and developed the synthesis of 2,7-methanobenzo[10]annulene-4,5-dicarboximides **7** (Figure 2).[5] Unfortunately, the increase of fluorescence quantum yield in **7** by the extension of the π-conjugation from was not observed.

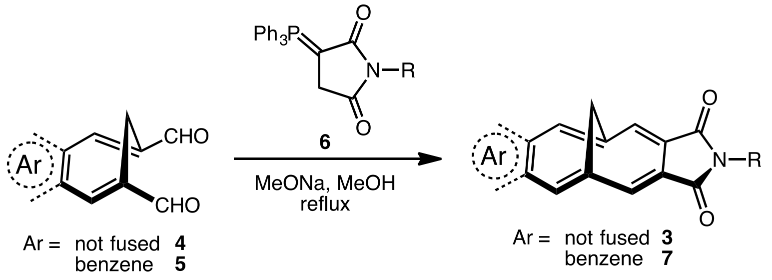


**Figure 2.** One-pot synthesis of **3** and **7** from dicarbaldehyde **4** and **5**

These results suggest that the photophysical behaviors of **3** and **7** are caused by 1,6-methano[10]annulene-3,4-dicarboximide skeleton. They prompt us to examine the improvement of the photophysical property for **7** and elucidation of their behavior. Bis(dicarboximide) **8** in which another dicarboximide skeleton is fused to the benzene moiety of **7** is worth investigating the photophysical property from the perspective of synergy effect of two types dicarboximide moiety (Figure 3). In this paper, we report the synthesis of ingenious bis(dicarboximide) **8** and describe the similar and its improved photophysical behavior of **8** with a comparison to **7**.

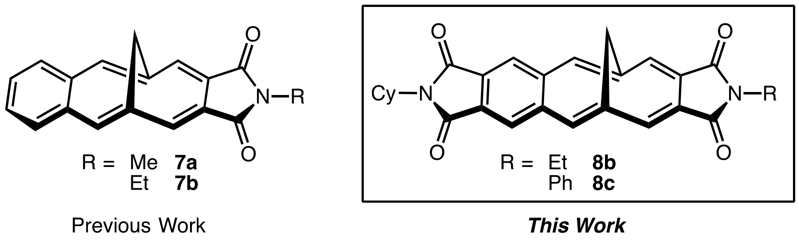
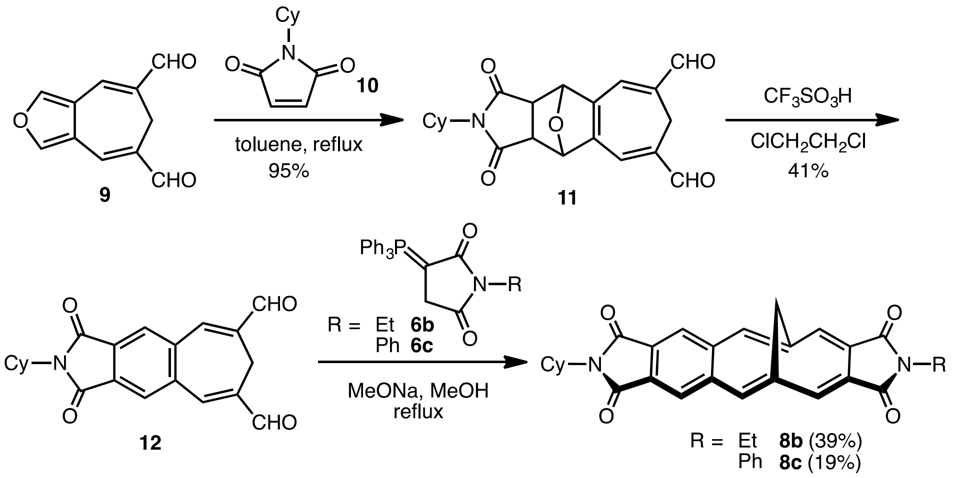


**Figure 3.** Synthetic targets of methanobenzo[10]annulene bisimides **8**

Synthetic route of **8** is summarized in Scheme 1. Ethyl and phenyl groups were installed on the dicarboximide to investigate the effects of the nitrogen-bound substituents on the photophysical character. On the other hand, cyclohexyl group was installed on another dicarboximide to improve solubility and to be synthesizable of **8**. In addition, the *N*-cyclohexyl-2,3-naphthalimide derivatives have displayed satisfactory fluorescence quantum yields, which will help improve the fluorescence quantum yield in **8**.[6] 6*H*-Cyclohepta[*c*]furan-5,7-dicarbaldehyde **9** was prepared by the condensation of 3,4-furandicarbaldehyde and glutaraldehyde.[7] Diels-Alder reaction of **9** with *N*-cyclohexylmaleimide **10** afforded **11** in accordance with the method reported by Nishina *et al.*[8] After the dehydration of **11**,[9] the target compounds **8** were synthesized by the reaction of **12** with triphenylphosphorane reagents **6** in a low yield.[5]



**Scheme 1.** Synthetic route of **8** from 6*H*-cyclohpeta[*c*]furan-5,7-dicarbaldehyde **9**

Structures of all new compounds were characterized by spectroscopic and high-resolution mass spectrometric analyses. Hydrogen atoms at the methylene bridge of **8** in their $^1H$ spectrum were shielded by the [10]annulene ring and slightly deshielded by the benzene ring, resulting in appearance at about $\delta$ 0.20 and 1.50 ppm. In the solid state IR spectra, compounds **8** exhibited two distinct carbonyl stretching bands of dicarboximide moieties at about 1750-1760 and 1700-1710 $cm^{-1}$ (**8b**: 1755, 1698 $cm^{-1}$; **8c**: 1761, 1709 $cm^{-1}$), because of weak two symmetric vibrations out of four vibrations. UV-Vis absorption and fluorescence emission spectra of **8** in $CH_2Cl_2$ are shown in Figure 4, and their photophysical properties are summarized in Table 1. As references, UV-Vis absorption and fluorescence emission spectra of **7** in $CH_2Cl_2$ were measured.[10] The molar extinction coefficients of bis(dicarboximide) **8** were larger than those of mono(dicarboximide) **7**, indicating that the increase of the light absorption area by annulation of bis(dicarboximide). The longest absorption wavelengths of **8** were slightly longer than those of **7** due to the slight decrease of the energy gap corresponding to the lowest excited states. On the other hand, those of **8b** and **8c** were comparable, suggesting that the transitions corresponding to the longest absorption wavelengths were attributed to the π-π* transitions on the methanobenzo[10]annulene skeleton. The fluorescence quantum yields *Φ* of **8b**, **8c** are comparable to each other and are about twice as large as those of **7a**, **7b** (**8b**: 28%, **8c**: 29%; **7a**: 16%, **7b**: 17%). In general, *N*-aryl-2,3-naphthalimides exhibit much weaker fluorescence compared to those of *N*-alkyl-2,3-naphthalimides because of the non-radiation decay of the excited state by the rotation of the phenyl groups (*N*-aryl: $\Phi < 1.0 \times 10^{-2}$%; *N*-alkyl: $\Phi >$ 1.0%).[11] However, *N*-phenyl-1,6-methano[10]annulene-2,3-dicarboximide (**3Ph**) displayed a weak fluorescence (*Φ* 8.5%) which was comparable to *N*-ethyl derivatives (*Φ* 9.6%),[4] suggesting that the decrease of the quantum yield was prevented by the annulene moiety.

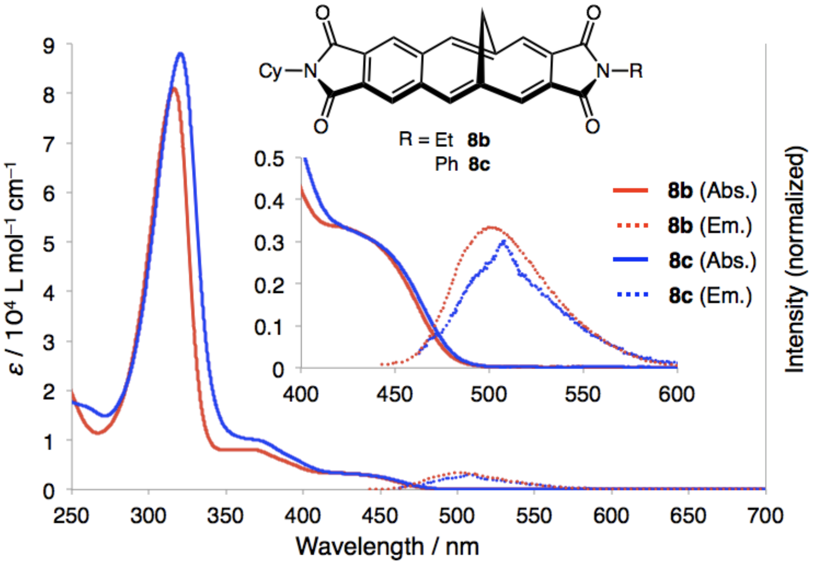


**Figure 4.** UV-Vis absorption and normalized fluorescence spectra of **8** (**8b**: $3.2 \times 10^{-5}$ M; **8c**: $2.9 \times 10^{-5}$ M)

**Table 1.** Photophysical data of **8** and **7**

| Compound | $\lambda_{abs}$ / nm | Log $\varepsilon$ / L mol$^{-1}$ cm$^{-1}$ | $\lambda_{em}$ / nm | Storks Shift / cm$^{-1}$ | *Φ* / % |
|---|---|---|---|---|---|
| **8b** (R = Et) | 420 | 3.53 | 499 | 3769 | 28 |
| **8c** (R = Ph) | 437 | 3.48 | 508 | 3198 | 29 |
| **7a** (R = Me) | 435 (sh.) | 2.86 | 513 | 3495 | 16 |
| **7b** (R = Et) | 436 (sh.) | 2.81 | 512 | 3404 | 17 |

Theoretical calculations were performed to investigate the effects of the annulation to bis(dicarboximide) and explain the relatively large quantum yields (see the Supporting Information for the detail and citation). Geometry optimization and TD-DFT calculations for **8b**, **8c**, and **7b** were carried out, and frontier Kohn-Sham orbitals were depicted in Figure 5. The experimentally observed IR spectroscopic parameters are satisfactorily reproduced by DFT calculations. Judged from the results of **8b** and **7b**, these electron density distributions did not change significantly. Similarly, although there is little experimental comparison between anthracene mono(dicarboximide) and bis(dicarboximide), its electron density distribution does not change significantly in theoretical calculations.[12] Therefore, the photophysical behavior of **8b** was similar to **7b**, and the simulated UV-Vis absorption spectra of **8b** and **7b** reproduced well the observed photophysical tendencies (Figure S17). Although the energy levels of molecular orbitals were stabilized by annulation to bis(dicarboximide), their energy gaps corresponding to the π-π* transitions did not change considerably, which was consistent with the slight increase in the longest absorption and emission wavelengths. According to TD-DFT calculations, the electronic transitions corresponding to the lowest excited states of **7**, **8** were assigned to the π-π* transitions on the 1,6-methanobenzo[10]annulene skeleton. However, the contribution of n-π* transitions derived from its relatively small molar extinction coefficients in the longest absorption wavelength of **7** could not be denied.[5] Similarly, for compounds **8**, the calculated oscillator strengths were considerably larger than those of **7**, whereas the smaller molar extinction coefficients compared to the other absorption bands suggested the possibility of the contribution of n-π* transitions. Although the electron densities in HOMO–1 of **8c** were localized to the phenyl group, the contribution of the charge transfer (CT) transition in the lowest excited state was smaller than those of π-π* transitions on the 1,6-methanobenzo[10]annulene skeleton. On the other hand, *N*-phenyl-2,3-naphthalimide (**1Ph**: Figure 1, R = Ph) with a small quantum yield shows a large contribution of the CT transition corresponding to the lowest excited state (see the Supporting Information). These findings revealed that the non-radiation decay in **8c** was less than that of **1Ph**, and its quantum yield did not decrease even at **8c**. In the comparison between **7b** and **8b**, the oscillator strength in the lowest excited state of **8b** was larger than that of **7b** by annulation to bis(dicarboximide), increasing the contribution of π-π* transition on the 1,6-methanobenzo[10]annulene skeleton.

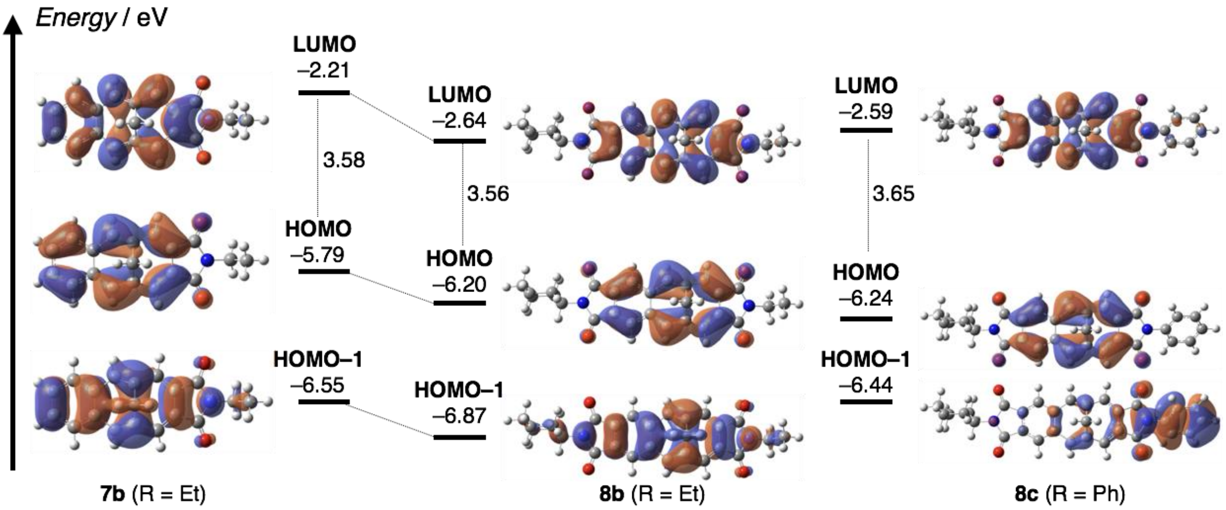


**Figure 5.** Frontier Kohn-Sham orbitals of **8b**, **8c**, and **7b** at the B3LYP/6-31G(d,p) level

In conclusion, the title methanobenzo[10]annulene-2,3:8,9-bis(dicarboximide) **8** were synthesized by the annulation of 6*H*-cyclohepta[*c*]furan with *N*-cyclohexylmaleimide and subsequent reaction with phosphorane reagents. Although annulation of another dicarboximide did not affect dramatically the absorption and emission wavelengths, their extinction coefficients and fluorescence quantum yields were improved. Theoretical calculation revealed that annulation to bis(dicarboximide) increased the contribution of π-π* transition on the annulene skeleton, leading to a large extinction coefficient for absorption and a large fluorescence quantum yield. Further studies on the substituent effects of the carboximides are now in progress.

## EXPERIMENTAL

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer by a KBr tablet method. UV-Vis spectra were measured on a Shimadzu UV-2550 spectrometer. Emission spectra were measured on a Shimadzu RT-5300PC spectrometer. $^{1}$H- and $^{13}$C- NMR spectra were recorded on a JEOL Lambda 400 or ECA 500 spectrometer. Chemical shift values of tetramethylsilane ($\delta$ = 0 ppm) were used as internal standards for $^{1}$H- and $^{13}$C- NMR spectra. Mass spectra were measured on a JMS-700 mass spectrometer. Column chromatography was performed with Silica gel 60 N from Kanto Chemical Co., Inc. All the manipulations were performed under a nitrogen atmosphere. Phosphorane reagents **6a** and **6b** were prepared according to a literature proceure.[5]

### Preparation of 11; Diels-Alder reaction of 6*H*-cyclohepta[*c*]furan-5,7-dicarbaldehyde (9) with *N*-cyclohexylmaleimide (10).

A mixture of 6*H*-cyclohepta[*c*]furan-5,7-dicarbaldehyde (**9**) (1.56 g, 8.29 mmol) and excess amount of *N*-cyclohexylmaleimide (**10**) (4.13 g, 23.0 mmol) in toluene (80 mL) was stirred under reflux for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The crude materials were purified by recrystallization from $CHCl_3$ and hexane to afford **11** as analytically pure solids (2.92 g, 7.95 mmol, 95%).

**11**: Ocher solids, mp 224-229 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.21-1.37 (m, 4H), 1.63-1.69 (m, 2H), 1.85 (d, 2H, $J$ = 12.4 Hz), 1.98 (d, 1H, $J$ = 13.7 Hz), 2.14 (qd, 2H, $J$ = 12.4, 3.9 Hz), 2.96 (s, 2H), 3.98 (tt, 1H, $J$ = 12.4, 3.9 Hz), 4.33 (d, 1H, $J$ = 13.7 Hz), 5.57 (s, 2H), 7.16 (d, 2H, $J$ = 1.0 Hz), 9.57 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.9, 25.0, 25.8, 28.8, 47.8, 52.6, 83.4, 133.2, 134.2, 148.9, 175.0, 189.7 ppm. UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$) = 241 (4.48), 355 (3.64), 383sh. (3.56), 408sh. (3.34), 426sh. (2.68) nm. MS (EI): $m/z$ (rel int.) = 367 ($M^+$, 11), 353 (7), 272 (8), 188 (100), 179 (24), 159 (94), 146 (12), 136 (22), 99 (31), 81 (19), 77 (21), 51 (8). HRMS (EI): Calcd. for $C_{21}H_{21}NO_5$ ($M^+$) 367.1420, found. 367.1423.

**Preparation of 12; Dehydration of Diels-Alder adduct 11.**

To a solution of **11** (118 mg, 0.321 mmol) in 1,2-dichloroethane (7 mL) was added trifluoromethanesulfonic acid (0.12 mL, 1.4 mmol) at 0 ºC. The reaction mixture was stirred for 1.5 h at room temperature. This reaction mixture was stirred further for 17 h under reflux. After cooling to room temperature, the mixture was poured into water (50 mL), and extracted with $CHCl_3$ (40 mL × 3). The combined organic layers were washed with a saturated $NaHCO_3$ aq. (100 mL) and with brine (100 mL), and then dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the crude materials were purified by silica gel chromatography [EtOAc/$CHCl_3$ (2:8)] to afford **12** as ocher solids (46 mg, 0.13 mmol, 41%).

**12**: Ocher solids, mp 195-199 ºC. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.25-1.43 (m, 3H, $J$ = 12.8 Hz), 1.71-1.77 (m, 3H, $J$ = 12.8 Hz), 1.90 (d, 2H, $J$ = 12.8 Hz), 2.23 (qd, 2H, $J$ = 12.8, 3.5 Hz), 3.27 (s, 2H), 4.16 (tt, 1H, $J$ = 12.8, 3.5 Hz), 7.47 (s, 2H), 7.98 (s, 2H), 9.65 (s, 2H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 17.7, 25.1, 26.0, 29.9, 51.6, 126.5, 132.1, 140.1, 142.2, 145.1, 167.1, 190.5 ppm. IR (KBr): $\nu_{CO}$ = 1714, 1672 cm$^{-1}$. UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$) = 271sh. (4.70), 279 (4.78), 336 (3.64) nm. MS (EI): *m/z* (rel int.) = 350 (23), 349 (M$^+$, 100), 306 (27), 280 (5), 268 (79), 250 (14), 238 (7), 167 (6), 139 (13). HRMS (EI): Calcd. for $C_{21}H_{19}NO_4$ (M$^+$) 349.1314, found. 349.1306.

**Synthesis of methanobenzo[10]annulene-2,3:8,9-bis(dicarboximide) (8b, 8c).**

A mixture of **12** (74 mg, 0.21 mmol), MeONa (23 mg, 0.43 mmol), and *N*-ethyltriphenylphosphoranylidenesuccinimide (**6b**) (127 mg, 0.328 mmol) in MeOH (10 mL) was stirred under reflux for 2 h. After cooling to room temperature, the mixture was poured into diluted HCl aq. (0.1 M, 40 mL), and extracted with $CHCl_3$ (40 mL × 3). The combined organic layers were washed with a saturated $NaHCO_3$ aq. (100 mL) and with brine (100 mL), and then dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the crude materials were purified by silica gel chromatography [EtOAc/$CHCl_3$ (1:9)] to afford **8b** (36 mg, 0.082 mmol, 39%).

Compound **8c** was synthesized by an analogous procedure as compound **8b** (yield: 12 mg, 0.025 mmol, 19%). Reagents: **12** (45 mg, 0.13 mmol), MeONa (14 mg, 0.26 mmol), **6c** (83 mg, 0.19 mmol).

**8b**: Yellow solids, mp 285-288 ºC. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 0.20 (d, 1H, $J$ = 10.9 Hz), 1.29 (t, 3H, $J$ = 7.2 Hz), 1.39 (m, 3H, $J$ = 12.6, 3.4 Hz), 1.50 (d, 1H, $J$ = 10.9 Hz), 1.73 (dm, 1H, $J$ = 12.6 Hz), 1.78 (dm, 2H, $J$ = 12.6 Hz), 1.90 (dm, 2H, $J$ = 12.6 Hz), 2.28 (qd, 2H, $J$ = 12.6, 3.4 Hz), 3.78 (q, 2H, $J$ = 7.2 Hz), 4.20 (tt, 1H, $J$ = 12.6, 3.4 Hz), 7.64 (s, 2H), 8.34 (s, 2H), 8.45 (s, 2H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 13.6, 25.1, 26.0, 29.8, 32.4, 33.6, 51.4, 127.2, 128.4, 128.7, 129.1, 129.8, 134.6, 137.6, 167.7, 168.4 ppm. IR (KBr): $\nu_{CO}$ = 1755, 1698 cm$^{-1}$. UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$) = 237 (4.41), 316 (4.91), 363 (3.91), 420 (3.53) nm. MS (EI): *m/z* (rel int.) = 440 (M$^+$, 21), 397 (28), 358 (100), 343 (29), 287 (20), 259

(19), 188 (18). HRMS (EI): Calcd. for $C_{27}H_{24}N_2O_4$ ($M^+$) 440.1736, found 440.1738.

**8c**: Yellow solids, mp >300 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 0.23$ (d, 1H, $J = 11.2$ Hz), 1.26-1.54 (m, 4H), 1.78 (dm, 3H, $J = 12.6$ Hz), 1.91 (d, 2H, $J = 12.2$ Hz), 2.29 (qd, 2H, $J = 12.2$, 3.6 Hz), 4.21 (tt, 1H, $J = 12.2$, 3.6 Hz), 7.39-7.53 (m, 5H), 7.70 (s, 2H), 8.47 (s, 4H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 25.1$, 26.0, 29.7, 29.8, 32.2, 51.4, 126.4, 127.3, 128.2, 128.4, 128.4, 129.1, 129.5, 129.7, 135.8, 137.6, 167.6, 167.7 ppm. IR (KBr): $\nu_{CO} = 1761$, 1709 cm$^{-1}$. UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$) = 233 (4.37), 320 (4.94), 371 (4.00), 437 (3.48) nm. MS (EI): *m/z* (rel int.) = 488 ($M^+$, 85), 445 (27), 406 (100), 389 (13), 362 (18), 259 (19), 188 (13). HRMS (EI): Calcd. for $C_{31}H_{24}N_2O_4$ ($M^+$) 488.1736, found. 488.1732.

## Determination of the quantum yield

The fluorescence quantum yields ($\Phi_x$) were determined by the equation (1) with reference to anthracene ($\Phi_{st} = 0.27$ in EtOH).[13]

$$\Phi_x = \Phi_{st} \frac{A_{st}}{A_x} \frac{F_x}{F_{st}} \frac{n_{st}^2}{n_x^2} \frac{I_{st}}{I_x} \frac{D_{st}}{D_x} \qquad (1)$$

Subscripts “x” and “st” stands for unknown and standard (anthracene) sample, respectively; $\Phi$ for quantum yield, $A$ for absorbance, $F$ for total area of the fluorescence spectra, $n$ for refractive index of the solvents, $I$ for intensity of the exciting light, and $D$ for dilution rate from the UV-Vis sample to the fluorescence sample. The values of $I_s/I_u$ were assumed 1 because the same exciting light was used. The refractive indices, $n = 1.42$ ($CH_2Cl_2$), 1.37 (EtOH) were used in correction.

## ACKNOWLEDGEMENTS

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9. Dehydration reaction of **11** using Sc(OTf)$_3$ in accordance with the method by reference 8, gave **12** in a low yield (21%).
10. UV-Vis absorption and fluorescence emission spectra of **7** are summarized in Supporting Information. Photophysical data of **7a** in MeOH were reported in reference 5 ($\lambda_{abs}$ = 436 nm, $\lambda_{em}$ = 527 nm, $\Phi$ = 10 %). No significant difference by solvents between MeOH and $CH_2Cl_2$ was observed.
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