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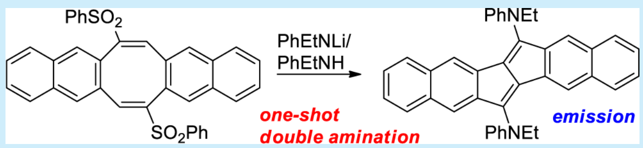
One-Shot Double Amination of Sondheimer–Wong Diynes: Synthesis of Photoluminescent Dinaphthopentalenes

Feng Xu,[†] Lifen Peng,[†] Kenta Shinohara,[†] Takanori Nishida,[†] Kan Wakamatsu,[‡] Motoyuki Uejima,[§] Tohru Sato,[§] Kazuyoshi Tanaka,*[,§] Norihiko Machida,[∥] Haruo Akashi,*[,∥] Akihiro Orita,*[,†] and Junzo Otera[†]

[†]Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama 700 0005, Japan
[‡]Department of Chemistry, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama 700 0005, Japan
[§]Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoyo 615 8510, Japan
[∥]Research Institute of Natural Sciences, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama 700 0005, Japan

Supporting Information

ABSTRACT: Photoluminescent diamino-substituted dinaphthopentalenes were synthesized successfully by the treatment of *in situ* prepared dinaphthocyclooctadiyne with lithium amide. This reaction involves a series of transformations including the nucleophilic addition of the lithium amide to a triple bond of the cyclooctadiyne moiety, transannulation, protonation of the resulting pentalene anion, and the nucleophilic substitution of the pentalene core with the lithium amide. In this procedure, a novel double amination step plays a key role. When the diamino-substituted dinaphthopentalenes were irradiated with UV light in toluene, fluorescence was observed at around 580 nm ($\Phi_F < 0.03$).



Expanded π-systems have attracted much attention because they can be used as the organic material in a range of useful devices such as organic light-emitting diodes (OLED), organic field effect transistors (OFET), and organic photovoltaic cells (OPV).[1] A number of polycyclic aromatic compounds have been synthesized, and their optoelectronic properties have been extensively explored. In recent times, much attention has been paid to antiaromatic compounds to explore new optoelectronic properties of extended π-systems and their applications.[2] In this context, synthetic methods for the preparation of arenopentalenes such as dibenzo- and dinaphthopentalenes have been developed,[3−8] and several derivatives of these materials have been applied in OFETs because of their relatively low-lying lowest unoccupied molecular orbital (LUMO) energy levels and small highest occupied molecular orbital (HOMO)−LUMO gaps.[4b,d] On the other hand, only a few pentalene derivatives exhibiting photoluminescence have been reported.[9] To explore the possibility of light-emitting pentalene, we performed time-dependent density functional theory (TD-DFT) calculations on the photoexcited transitions of several dibenzo- and dinaphthopentalenes (Figure 1). The calculations demonstrated that diamino-substituted dinaphthopentalene **1a** exhibits a positive oscillator strength for the first transition (f = 0.300), which is mainly composed of the HOMO−LUMO transition (69.3%), giving rise to the possibility of photoluminescence in **1a**. In sharp contrast, the HOMO−LUMO transition is prohibited in dinaphthopentalene **2** and dibenzopentalenes **3a** and **4**; the oscillator strengths (f) of the first transition for **2**, **3a**, and **4** are zero.

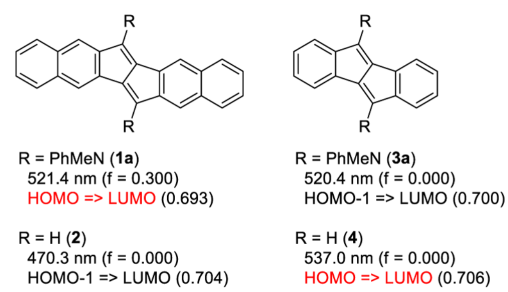


Figure 1. Structures of pentalenes and calculated wavelengths of photoexcitation.

Transition-metal-catalyzed couplings are most commonly used for the synthesis of arenopentalenes.[4] Saito synthesized bis(trimethylsilyl)-substituted dibenzopentalene by the reduction of trimethylsilylethynylbenzene with lithium and successfully isolated the di- and monoanions of dibenzopentalene.[5] More recently, Xi synthesized a variety of pentalenes by treating 1,4-diiodo-1,3-butadiene with t-BuLi/Ba$[N(SiMe_3)_2]_2$[7a] and Rieke Ca.[7b] We reported new methodologies for the syntheses of 5,10-unsymmetrically substituted dibenzopentalenes by successive additions of a nucleophile and an electrophile to dibenzocyclooctadiyne **5** (Sondheimer−Wong diyne)[10] (reaction 1 in Scheme 1)[8a] and by nucleophilic substitution of halo-substituted pentalene **6** (reaction 2).[8c]

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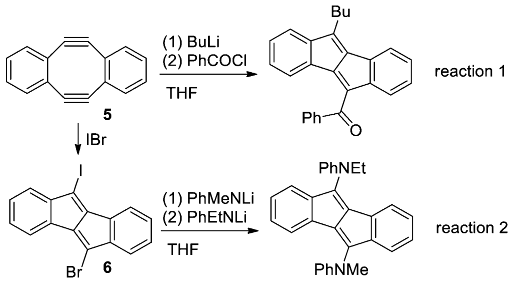
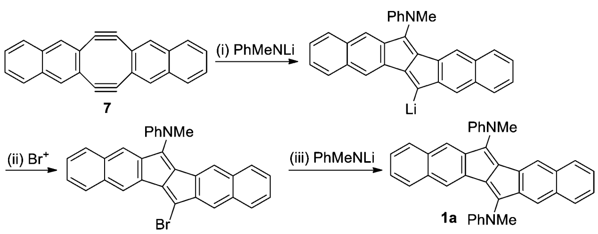
Scheme 1. Syntheses of 5,10-Substituted Dibenzopentalenes



Our initial synthetic plan for **1a** using dinaphthocyclooctadiyne **7** as a starting compound is shown in Scheme 2. This

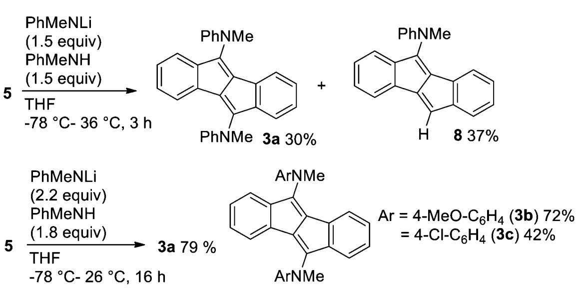
Scheme 2. Initial Synthetic Plan for 1a



synthetic route of **1a** involves three transformations: (i) nucleophilic addition of lithium amide to the alkyne moiety of **7** followed by transannulation; (ii) bromination of the resulting pentalene anion (similar to reaction 1); and (iii) substitution of the bromine with lithium amide (similar to reaction 2).

To optimize the reaction conditions for step (i), dibenzocyclooctadiyne **5** was treated with lithium methyl(phenyl)amide as a model reaction (Scheme 3). Surprisingly,

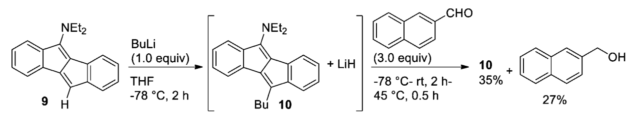
Scheme 3. Double Amination of 5



when 1.5 equiv of PhMeNLi and PhMeNH were added to a THF solution of **5**, diamino-substituted dibenzopentalene **3a** was obtained in 30% yield along with the expected monoamine derivative **8** (37%). When the reagent amounts were increased (PhMeNLi (2.2 equiv)/PhMeNH (1.8 equiv)), **3a** was obtained as the sole product in 79% yield. Similarly, methoxy- and chloro-substituted derivatives **3b** and **3c** were synthesized in 72% and 42% yields, respectively.

To shed light on the mechanism of this novel double amination, diethylamino pentalene **9** was treated with 1.0 equiv of BuLi followed by 3.0 equiv of 2-naphthaldehyde (Scheme 4). In this reaction, butyl- and diethylamino-substituted pentalene **10** and 2-naphthyl methanol were obtained in 35% and 27% yields, respectively. Because the latter product could be prepared from the reduction of 2-naphthaldehyde, it is assumed

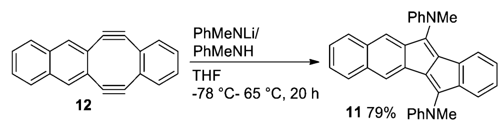
Scheme 4. Elimination of LiH in Substitution of 9



that, in the substitution of diethylamino pentalene **9** with BuLi, lithium hydride might have been generated, which then reduced the aldehyde.[11,12]

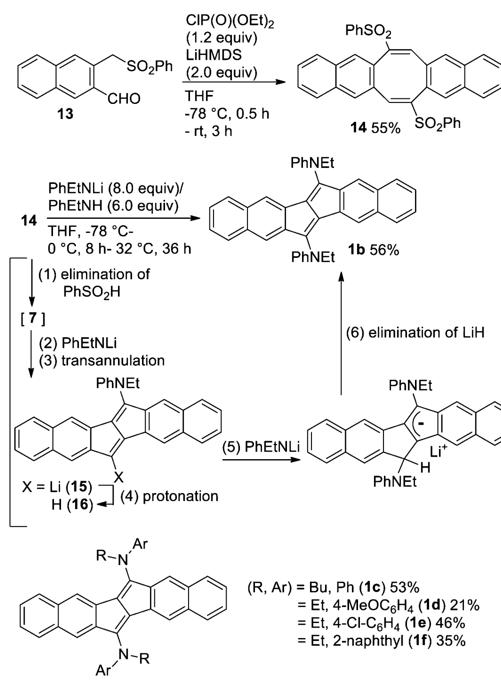
This double amination protocol also served in the synthesis of diamino-benzonaphthopentalene **11**. When benzonaphthocyclooctadiyne **12** was treated with lithium methyl(phenyl)amide, the desired pentalene **11** was obtained in 79% yield (Scheme 5).

Scheme 5. Double Amination of 12



In light of these preliminary results, the addition of lithium ethyl(phenyl)amide to dinaphthocyclooctadiyne **7** was investigated (Scheme 6). Because dinaphthocyclooctadiyne **7** is

Scheme 6. One-Shot Synthesis of 1b



poorly soluble due to its highly expanded π-system,[13] **7** was generated *in situ* by treating the cyclic vinylsulfone precursor **14** with lithium amide. Thus, the diyne obtained was used in the following transformations without purification.[14] When the cyclic vinylsulfone **14**, which had been prepared from the corresponding formylsulfone **13**, was treated with PhEtNLi (8.0 equiv)/PhEtNH (6.0 equiv) in THF, the desired diamino-substituted dinaphthopentalene **1b** was obtained in 56% yield. Remarkably, the process, which was composed of a series of transformations including (1) the elimination of $PhSO_2H$ affording dinaphthocyclooctadiyne **7**, (2) the addition of

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PhEtNLi to the *in situ*-prepared dinaphthocyclooctadiyne **7** followed by (3) the subsequent transannulation, (4) the protonation of the resulting pentalene anion **15**, (5) the nucleophilic addition of PhEtNLi to the resulting pentalene **16**, and (6) the elimination of lithium hydride, proceeded smoothly in a one-shot manner. It should be noted that the 56% overall yield in the six steps corresponds to an average yield of 91% for each step despite the demanding reaction conditions. By changing the lithium amide, the corresponding diamino-substituted dinaphthopentalenes **1c**–**f** were obtained in moderate yields. The structure of bisaminopentalene **1b** was confirmed by single-crystal X-ray analysis (Figure S1). The bisaminopentalene **1b** exhibits a monoclinic crystal system (*P*21/*n*) with the center of symmetry residing on the midpoint of C1–C1′.

The UV–vis absorption spectra of these four pentalenes **1c**–**f** were recorded in CH_2Cl_2 (Figure 2). Table 1 summarizes the

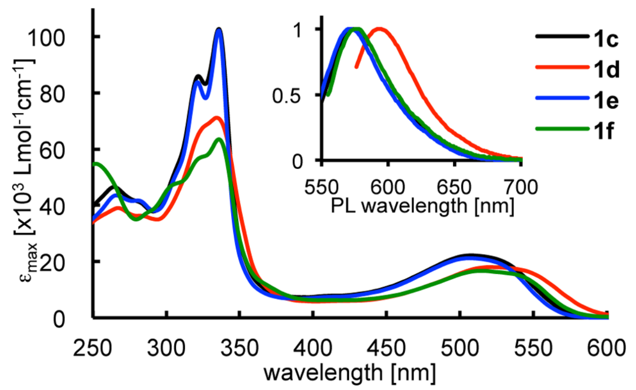

Figure 2. UV–vis absorption (CH_2Cl_2, 1.0 × 10^{-4} M) and photoluminescence spectra (inset, toluene, 9.7 × 10^{-7} M) of **1c**–**f**.

spectral data and their plausible excitation wavelengths along with the oscillator strengths, which were calculated for the first excitation energies at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level. All the derivatives **1c**–**f** exhibited weak and strong absorption bands centered at around 510 (ε < 23 × 1000) and 336 nm (ε > 63 × 1000), respectively. The methoxy phenyl- and naphthyl-substituted derivatives **1d** and **1f** exhibited slight bathochromic shifts in comparison with **1c** and **1e**; for instance, the longest wavelength of the absorption bands were observed at 519 and 514 nm for **1d** and **1f**, respectively, and at 507 and 506 nm for **1c** and **1e**, respectively. These absorption bands around 510 nm were consistent with the calculated wavelengths for the first excitation of **1c**–**f** and could thus be characterized as HOMO–LUMO transitions within these molecules.

As the *ab initio* calculations suggested that HOMO–LUMO transitions were allowed in **1c**–**f**, their photoluminescence spectra were recorded. When the dinaphthopentalenes **1c**–**f** were irradiated with UV light in toluene, all the derivatives emitted fluorescence, although the emission quantum yields were less than 0.03. The emission maxima of **1c**, **1e**, and **1f** were observed around 580 nm, and the emission of methoxyphenyl derivative **1d** was at 594 nm (Figure 2 inset, Table 1). To gain further insight into the photochemistry of **1c**–**f**, the HOMO and LUMO of **1a** were investigated at the B3LYP/6-31G(d) level. The results indicated that, in **1a**, the HOMO was expanded over the dinaphthopentalene moiety and two phenyl groups through the lone pairs of amino nitrogens (Figure 3a). In contrast, the LUMO orbital was

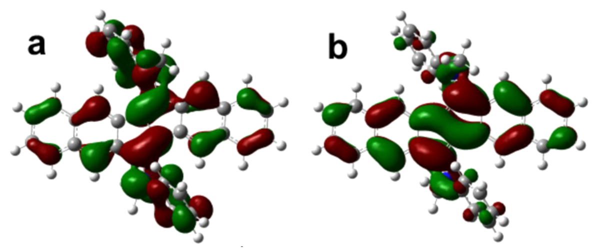

Figure 3. (a) HOMO and (b) LUMO of **1a**.

located mainly on the dinaphthopentalene core (Figure 3b). Fragment molecular orbital (FMO) analysis revealed that the HOMO(135) of **1a** was composed by a linear combination of the HOMO(78) of the dinaphthopentalene (DNP) fragment and the LUMO(58) of a pair of PhMeN fragments, while the LUMO(136) of **1a** was composed by the LUMO+1(80) of DNP and HOMO(57) of PhMeN fragments (Figure S2). In **1a**, the symmetries of the HOMO and LUMO are a_g and a_u, respectively, and the HOMO–LUMO transition (S1, A_u) is allowed, enabling the photoluminescence of **1c**–**f**.[15] Nucleus-independent chemical shifts (NICS(1)) were also computed to survey the (anti)aromaticity in **1a** (Figure S3). Naphtho moieties maintained the aromaticities (NICS(1) values = −10.3, −8.2), and the pentalene core maintained antiaromaticity despite the substitution of a pair of amino groups (NICS(1) values = 1.4).[16]

In summary, photoluminescent diamino-substituted pentalenes were synthesized. The synthesis was realized by employing Sondheimer–Wong diynes as key starting materials. The integration of six steps including a novel diamination process led to the straightforward synthesis of the desired compounds. Thus, the bisaminopentalenes obtained emitted photoluminescence when irradiated with UV light in toluene. Further synthesis of the amino-pentalenes and their application to organic materials is under investigation, particularly with the aim of increasing the quantum yield of photoluminescence.

Table 1. Summarized UV–vis Absorption[a] and Photoluminescence[b] Data and TDDFT Calculations[c] of 1c–f

	1c	1d	1e	1f
λ_{max} [nm] (ε_{max} ×1000 [L mol^{-1} cm^{-1}])	507 (22)	519 (18)	506 (21)	514 (17)
	336 (103)	334 (71)	336 (102)	336 (63)
first excitation [nm] (f)[d]	521 (0.30)	544 (0.30)	522 (0.31)	531 (0.70)
E_{max}[e] [nm]	575	594	572	577

[a]In CH_2Cl_2, 1.0 × 10^{-4} M. [b]In toluene, 9.7 × 10^{-7} M. [c]Calculations were performed for the corresponding ArMeN derivatives at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level. [d]Oscillator strength f. [e]Photoluminescence quantum yields (Φ_F) of **1c**–**f** were <0.03.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization of all the products, DFT results, oxidation and reduction potentials, and crystallographic data for **1b** (CIF, CCDC 1011864). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01293.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ktanaka@moleng.kyoto-u.ac.jp.
*E-mail: akashi@rins.ous.ac.jp.
*E-mail: orita@dac.ous.ac.jp.

Notes

The authors declare no competing financial interest.

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(15) Oxidation and reduction potentials electrochemically recorded for **1c-f**, **3a**, and **11** were shown in the Supporting Information.

(16) Calculations of NICS(1) values for dinaphthopentalene presented 2.5 for the pentalene core and −7.1 and −10.0 for the naphtho moieties.

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