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Optical and electronic properties of siloxane-bridged cyclic dimers with naphthylene or pyrenylene moieties

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ABSTRACT

The optical and electronic properties of novel siloxane-bridged cyclic dimers with naphthylene (**CD1**) or pyrenylene (**CD2**) moieties are described. **CD1** and **CD2** were obtained by the cyclic dimerization of 1,4-bis(dimethylhydroxysilyl)naphthalene (**M1**) and 1,6-bis(dimethylhydroxysilyl)pyrene (**M2**), respectively. **CD1** and **CD2** mainly exhibited the emission from their excimers owing to their short distances between aryl moieties in **CD1** and **CD2**, which were determined to be 3.44 Å and 3.41 Å by the X-ray crystallographic analysis, respectively. The absorption spectra of **CD2** in the presence of 7,7,8,8-tetracyanoquinodimethane (TCNQ) revealed that **CD2** has the ability to form 1:1 charge-transfer complex with TCNQ, indicating the existence of the transannular π–π interaction between closely located pyrene components in **CD2**.

1. Introduction

Cyclophanes are unique cyclic compounds containing aromatic moieties bridged by methylene moieties.[1] For their unique structures, cyclophanes have much attracted interests in polymer science,[2] organometallic chemistry,[3] biology,[4] and molecular recognition chemistry[5] for application, such as chiral catalysts[6] and optoelectronic materials.[7] Many cyclophane-based compounds containing various aromatic moieties, such as naphthalene (naphthalenophane),[8] anthracene (anthracenophane),[9] or pyrene (pyrenophane),[10] have been reported for the investigation of the unique molecular recognition behavior and the optical or electronic property. On the other hand, cyclophane compounds bridged by siloxane bondings have been reported to attract much attention because of their unique optical and electronic properties based on the σ*–π* conjugation between silylene moiety and aromatic one.[11] For instance, it has been reported that the introduction of alkyl silyl moieties onto aromatic compounds induces some interesting effects such as the red-shift of the maximum absorption and fluorescence together with the enhancement of the emission efficiency.[11] The siloxane-bridged cyclic dimers containing benzene,[12] thiophene,[12] pyridine,[12] and stilbene[13] skeletons have been reported for the study of their electron transfer processes between siloxane-bridged aromatic structures. As for the optical properties of siloxane-bridged cyclic dimers, the silacyclophane containing stilbene moieties has only been reported to show the red-shift of absorption and emission as well as the high emission efficiency; however, the emission from the excimer has not been reported. On the other hand, siloxane-bridged cyclic dimers can be considered to be the analogous compounds of [3.3]cyclophane derivatives. Several reports[14] on [3.3]cyclophane-like compounds have been made, where the structural and conformational analysis and the reaction of [3.3]cyclophane-like compounds were mainly described; however, there have been few reports[14a] on the optical or electronic properties of [3.3]cyclophane-like compounds.

Thus, we have been interested in the structural features of siloxane-bridged cyclic dimers and both optical and electronic effects of silylene moieties attached to aromatic moiety. Here, we report the synthesis of novel siloxane-bridged cyclic dimers having naphthylene (**CD1**) or pyrenylene (**CD2**) moieties to reveal their optical and electronic properties. The unique emission behavior of **CD1** and **CD2**, that is, the emission of **CD1** and **CD2** resulted from the excimer will be revealed. In addition, the high electron-donating ability of **CD2** will be also revealed from the investigation for the formation of charge-transfer (CT) complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ).

2. Results and discussion

2.1. Preparation of cyclic dimers

Scheme 1 shows cyclic dimerization of bis(dimethylhydroxysilyl)aromatic compounds, **M1**[15] and **M2**,[16] using 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate as a catalyst in dilute solution

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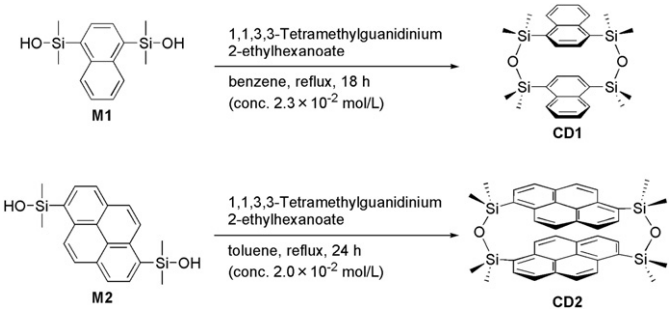
(see Experimental parts) to afford two siloxane-bridged cyclic dimers, **CD1** (yield: 37.8%) and **CD2** (yield: 44.6%), respectively. This condensation reaction afforded the large-number-membered cyclic compounds, such as cyclic trimer and tetramer, besides the cyclic dimer; however, the cyclic dimers were easily purified by recrystallization. Too high concentration of **M1** or **M2** for the present condensation has been reported to result in the corresponding polymer formation.[15,16]



Scheme 1. Synthesis of siloxane-bridged cyclic dimers, **CD1** and **CD2**.

2.2. Optical characterization

Figure 1 shows the absorption and fluorescence spectra of naphthalene-based and pyrene-based derivatives.

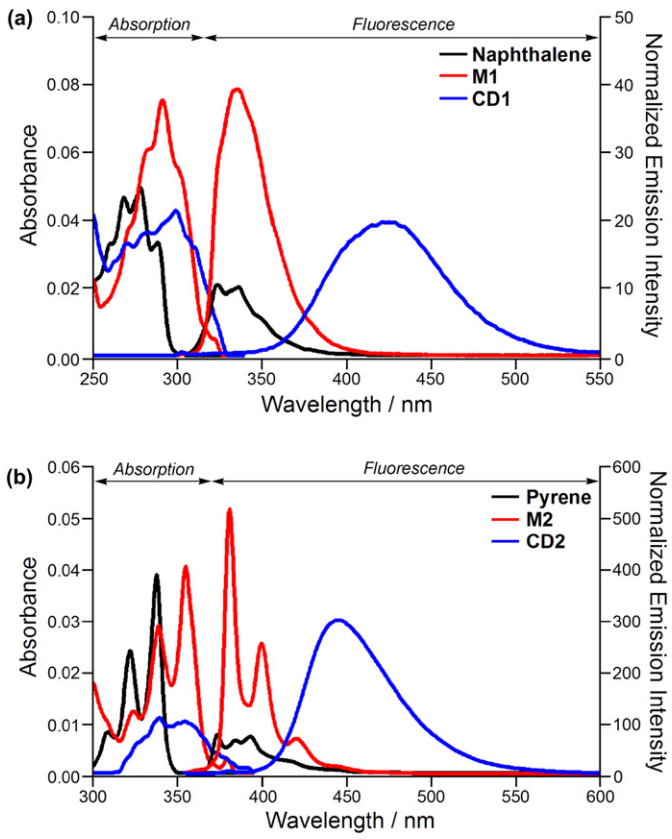


Figure 1. Absorption and fluorescence spectra of (a) naphthalene derivatives (concn 1.0×10^{-5} mol/L per monomer unit, λ_{ex}: 278 nm); (b) pyrene derivatives (concn 1.0×10^{-6} mol/L per monomer unit, λ_{ex}: 338 nm) in $CHCl_3$ at ambient temperature. The values of the vertical axis in the case of fluorescence spectra were normalized using the molar extinction coefficient of each compound at λ_{ex}.

In all present absorption spectra, bathochromic and hyperchromic effects were observed by the introduction of silylene groups onto naphthalene and pyrene skeletons, presumably because of σ–π and σ*–π* conjugations between the silylene groups and aromatic moieties.[11] The bathochromic effect has been known to be induced by lowering the energy gap between the HOMO and LUMO states because of both destabilization of HOMO state through σ–π conjugation and stabilization of LUMO state through σ*–π* conjugation. The hyperchromic effects would be resulted from the enhancement of transition moment based on the increase in the dipole moments of the HOMO and LUMO states owing to the σ–π conjugation in the HOMO and the σ*–π* conjugation in the LUMO. On the other hand, the molar extinction coefficients of **CD1** and **CD2** were found to be smaller than those of the corresponding bis(dimethylhydroxysilyl)aromatic compounds, owing to the offset of the transition moments of two aromatic moieties in cyclic compounds. Figure 1 also indicates the increase in fluorescence intensity of **M1** and **M2** compared with that of naphthalene and pyrene, respectively, that is, the introduction of silylene groups onto naphthalene and pyrene induced the enhancement of emission intensity.

Furthermore, the broad and structureless emission bands were observed in the fluorescence spectra of **CD1** and **CD2**, which would be due to the excimer emission as deduced from their excitation spectra as shown in Figure 2. Table 1 summarizes the optical characterization of naphthalene and pyrene derivatives. The fluorescence quantum yield (Φ_F) was improved by the introduction of the silylene groups onto aromatic moieties. In addition, the Φ_Fs of **CD1** and **CD2** were higher than those of **M1** and **M2**, respectively, because of the relatively efficient emission from their excimers.

2.3. X-ray crystallographic analysis

For the clarification of the reason for the efficient emission from the excimer in the case of **CD1** and **CD2**, we achieved the X-ray crystallographic analyses of **CD1** and **CD2**. Table 2 shows the crystal data and refinement parameters for the X-ray crystallographic analyses of **CD1** and **CD2**.

Figure 3 depicts the ORTEP views of one molecule of **CD1** and **CD2**. The inter-ring distances in **CD1** and **CD2** were determined to be 3.44 Å and 3.41 Å, respectively.

Furthermore, it turned out that the two aromatic rings in **CD1** and **CD2** do not overlap precisely each other as reported[12] that the two thiophene rings adopt the *anti* conformation in the siloxane-bridged thiophenophane. The close location of aromatic rings in **CD1** and **CD2** would result in the efficient emission from the excimers as observed in the emission spectra.

2.4. CT complex formation with TCNQ

Next, the electronic properties of **CD1** and **CD2** were investigated via the CT complex formation with TCNQ. It has been well-known that cyclophane compounds possess the electron-donating ability to form the CT complexes with TCNQ.[18] On the other hand, the pyrene derivative with strong electron-donating groups, such as 1,3,6,8-tetrakis(dimethylamino)pyrene has also been reported to form CT complex with TCNQ efficiently.[19] We also confirmed that the CT complex formation of pyrene or **CD2** with TCNQ by the absorption spectral change of pyrene or **CD2** in the presence of TCNQ as shown in Figure 4. The new absorption band in the range of 600–1000 nm depending on the ratio of pyrene or **CD2** to TCNQ appeared in the absorption spectra of pyrene or **CD2** in the presence of TCNQ, indicating the CT complex formation of pyrene or **CD2** with TCNQ.

On the other hand, no CT absorption bands were observed in the absorption spectra of naphthalene or **CD1** in the presence of TCNQ

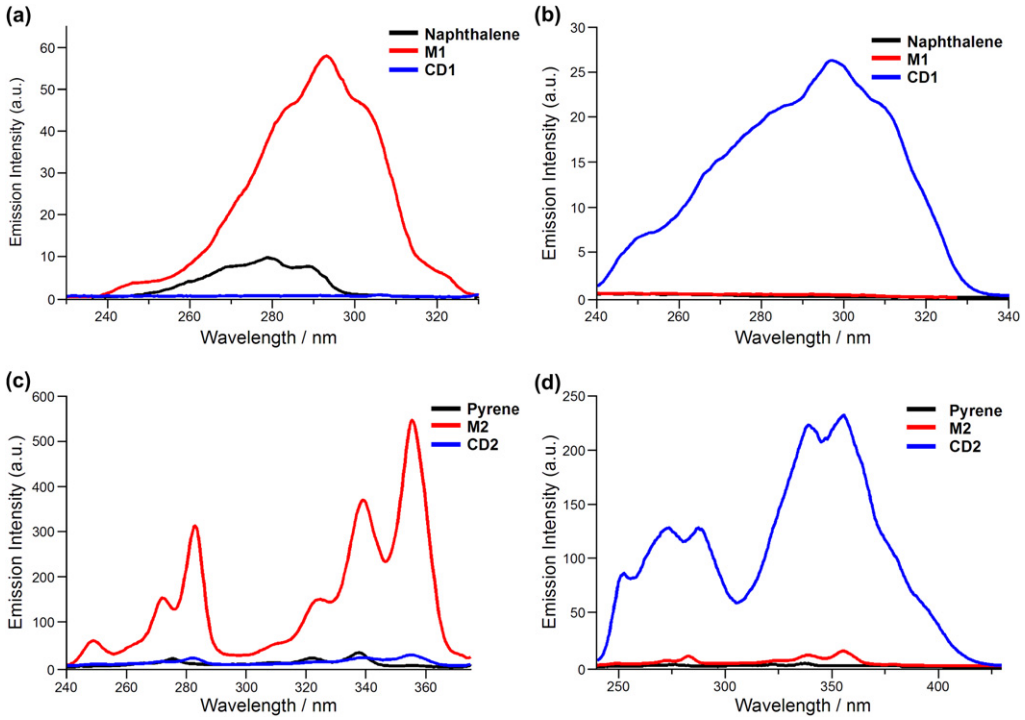


Figure 2. Excitation spectra of naphthalene derivatives (concn 1.0×10^{-5} mol/L per monomer unit, λ_{em}: (a) 337 nm, (b) 430 nm); pyrene derivatives (concn 1.0×10^{-6} mol/L per monomer unit, λ_{em}: (c) 380.5 nm, (d) 445.5 nm) in $CHCl_3$ at ambient temperature.

Table 1
Optical characterization of naphthalene and pyrene derivatives

Compound	λ_{abs}/nm (ϵ/L mol^{-1} cm^{-1})	λ_{em}/nm	Φ_F[a]
Naphthalene	269 (4600)	324	0.03
	278 (5000)	336	
	289 (3300)		
M1	283 (6100)	337	0.11
	291 (7600)		
	300 (5600)		
CD1	271 (3300)	422	0.22
	299 (4300)		
	309 (3200)		
Pyrene	309 (8000)	374	0.19
	322 (23,600)	385	
	338 (38,200)	393	
M2	324 (12,000)	381	0.50
	339 (28,400)	400	
	355 (42,000)	421	
CD2	340 (10,500)	445	0.54
	355 (10,000)		

[a] Fluorescence quantum yields (Φ_F) of naphthalene (λ_{ex}=278 nm) and pyrene (λ_{ex}=338 nm) derivatives were measured in $CHCl_3$ using a HAMAMATSU PHOTONICS absolute PL quantum yield measurement system C9920-02.[17]

probably because of too low concentration of naphthalene or **CD1**; though the crystal structure of naphthalene-TCNQ (1:1) complex[20] and its enthalpy for the CT complex formation[21] have been reported. This result would mean that naphthalene and **CD1** have the lower ability to form CT complexes with TCNQ than pyrene and **CD2**.

In addition, Figure 5 depicts the Job's plots[22] for the formation of CT complexes with pyrene or **CD2**. In both cases, the chloroform solution of the equimolar ratio of pyrene derivatives to TCNQ gave the maximum absorbance at the wavelength for the CT complex formation, meaning that pyrene and **CD2** form 1:1 CT complexes with TCNQ. This finding means that the other pyrene moiety in **CD2** would not have the sufficient electron-donating ability to form the CT complex with TCNQ when a pyrene moiety of **CD2** forms the CT complex with TCNQ, probably because the

Table 2
Crystal data and refinement parameters for the X-ray crystallographic analyses of **CD1** and **CD2**

Crystal parameters	**CD1**	**CD2**
Chemical formula	$C_{28}H_{36}O_2Si_4$	$C_{40}H_{40}O_2Si_4$
Formula weight	573.03	665.08
Temperature, K	90	90
Crystal system	Triclinic	Monoclinic
Space group	*P*1	*P*2(1)
a, Å	8.8856	11.2399
b, Å	11.7531	11.3711
c, Å	13.8314	26.6731
α, degree	80.41	90.00
β, degree	89.58	96.806
γ, degree	77.73	90.00
Volume, Å^3	1391.1	3385.1
Z	2	4
Density (calculated), Mg/m^3	1.368	1.305
Crystal size, mm^3	0.40×0.30×0.15	0.20×0.20×0.01
λ (Mo Kα), Å	0.71073	0.71073
Reflections collected	6697	8924
Independent reflections	5702	4984
G.O.F.	1.003	1.055
R_1, wR_2, ($I>2\sigma$ (I))	0.0437, 0.0964	0.0500, 0.1058
R_1, wR_2, all data	0.0558, 0.1045	0.0849, 0.1301

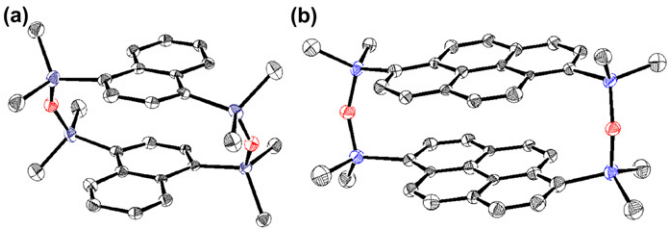


Figure 3. ORTEP views of one molecule of (a) **CD1** and (b) **CD2** with thermal ellipsoids (50% probability). The hydrogen atoms are omitted for clarity. Silicon and oxygen atoms are highlighted in blue and red, respectively.

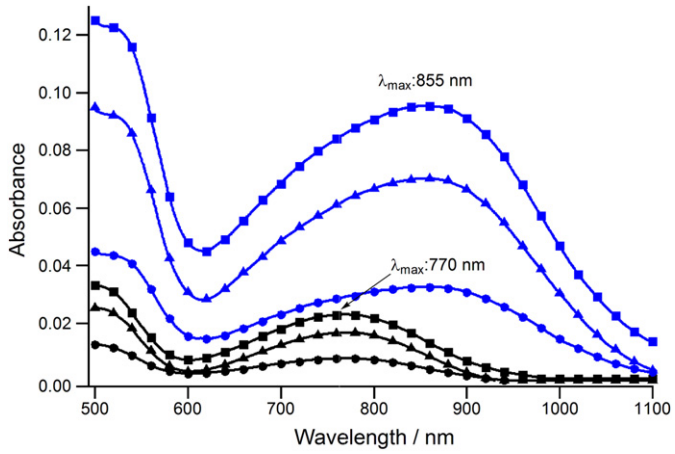


Figure 4. Absorption spectra of pyrene (black line) and **CD2** (blue line) in the presence of TCNQ in $CHCl_3$ at 20 °C. Total concentration ([pyrene]+[TCNQ] or [**CD2**]+[TCNQ]) was fixed at 20 mmol/L. Molar ratios of pyrene or **CD2** toward TCNQ were 0.1(●), 0.5 (■), and 0.7(▲).

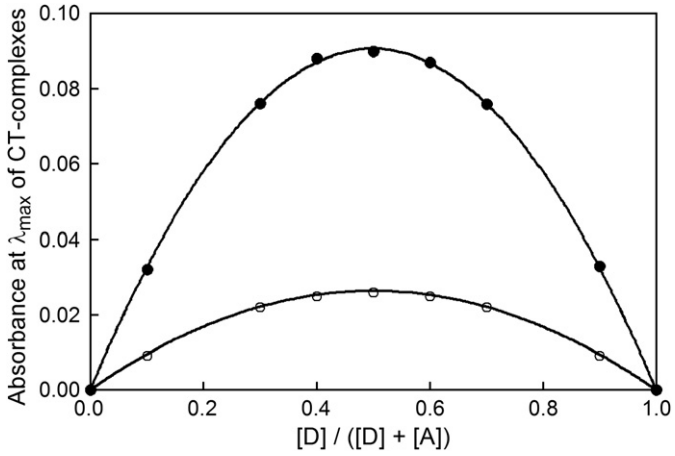


Figure 5. Job's plot for the complexation of pyrene (○) or **CD2** (●) with TCNQ. [D] represents [pyrene] or [**CD2**], and [A] does [TCNQ]. Total concentration of [D]+[A] was maintained at 20 mmol/L.

electron-donating ability of the pyrene in **CD2** would be decreased by the through-space conjugation induced by the CT complex formation of another pyrene moiety in **CD2** with TCNQ. The maximum CT absorption was observed at 855 nm in the absorption spectra of **CD2** in the presence of TCNQ, whereas it was observed at 770 nm in those of pyrene in the presence of TCNQ. Namely, the transannular π–π interaction between closely located pyrene components in **CD2** decreased the CT transition energy resulting in a bathochromic shift.

The CT transition is considered to occur from the HOMO energy level of the electron-donating moiety to the LUMO energy level of the electron-accepting one. Thus, we calculated the HOMO energy levels of naphthalene, **CD1**, pyrene, and **CD2** with density-functional theory (DFT) method at the B3LYP/6-31G(d) level of theory.

Table 3 summarizes the wavelength at maximum CT absorption and the HOMO energy levels of naphthalene, **CD1**, pyrene, and **CD2**, and the energy diagrams are depicted in Figure 6. The HOMO energy level of **CD2** (−5.17 eV) was higher than that of pyrene (−5.33 eV), indicating that the energy difference between the HOMO energy level of **CD2** and the LUMO energy level of TCNQ (−4.82 eV) is smaller than that between the HOMO energy level of pyrene and the LUMO energy level of

Table 3
Wavelength at maximum CT absorption with TCNQ and HOMO levels of naphthalene, **CD1**, pyrene, and **CD2** at the B3LYP/6-31G(d) level of theory

Compound	λ_{max} of CT[a]/nm	HOMO[b]/eV
Naphthalene	—[c]	−5.79
CD1	—[c]	−5.58
Pyrene	770	−5.33
CD2	855	−5.17

[a] Wavelength at maximum CT absorption with TCNQ in $CHCl_3$.
[b] Calculated with density-functional theory (DFT) method at the B3LYP/6-31G(d) level of theory.
[c] Not observed.

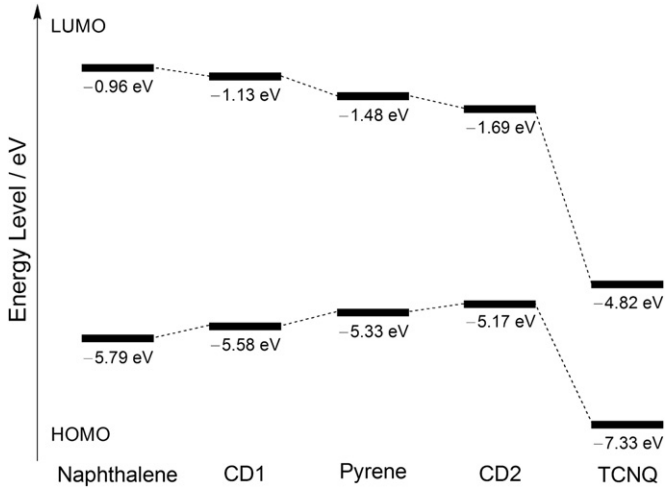


Figure 6. Energy diagrams of naphthalene, **CD1**, pyrene, **CD2**, and 7,7,8,8-tetracyanoquinodimethane (TCNQ). Calculated using DFT method at the B3LYP/6-31G(d) level.

TCNQ. This result is in agreement with the observation of the bathochromic shift in the case of CT complex of **CD2** with TCNQ compared with that of pyrene with TCNQ. In contrast, naphthalene and **CD1** would not form the CT complex with TCNQ as deduced from the absorption spectra of naphthalene or **CD1** in the presence of TCNQ. The difference in the energy level between the HOMO of naphthalene (−5.79 eV) or **CD1** (−5.58 eV) and the LUMO of TCNQ is too large to form the CT complexes under the present conditions.

3. Conclusion

We achieved the synthesis of novel siloxane-bridged cyclic dimers with naphthylene (**CD1**) or pyrenylene (**CD2**) moieties. **CD1** and **CD2** mainly exhibited the emission from their excimers with high efficiency for very close location of aryl moieties in **CD1** and **CD2**. The absorption spectra of pyrene or **CD2** in the presence of TCNQ revealed that pyrene and **CD2** has the ability to form 1:1 CT complex with TCNQ. In addition, the energy difference between HOMO of **CD2** and LUMO of TCNQ was smaller than that between HOMO of pyrene and LUMO of TCNQ. These results concerning the CT complex formation indicate that the very close location of two pyrene components in **CD2** enables a transannular π–π interaction between two pyrene components.

4. Experimental

4.1. General experimental procedures

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400F spectrometer in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide [$(CD_3)_2SO$] at ambient temperature. IR spectra were

measured on a Perkin–Elmer Spectrum One FT-IR spectrometer. Melting point was determined by differential scanning calorimetry (DSC) on a RIGAKU ThermoPlus DSC8230 at a heating rate of 10 °C/min under a nitrogen flow rate of 10 mL/min. Gas chromatography/mass spectroscopy (GC/MS) was carried out using a Shimadzu GCMS-QP2020A instrument. Absorption spectra were measured on a Shimadzu UV-2450 or JASCO UV510 spectrophotometer. Fluorescence and excitation spectra were measured on a Shimadzu RF-5000s spectrometer by use of the chloroform solution degassed by argon bubbling for 30 min. Fluorescence quantum yield of pyrene and naphthalene derivatives were measured using a HAMAMATSU PHOTONICS C9920-20 absolute PL quantum yield measurement system.[17]

4.2. X-ray crystallographic analysis

X-ray crystal structures were measured using Bruker APEX II CCD area detector (Mo Kα, λ=0.71073 nm). X-ray quality crystals of **CD1** and **CD2** were obtained by recrystallization from vapor diffusion of tetrahydrofuran and CH_2Cl_2. The crystals were dried under reduced pressure and a suitable crystal was selected. Molecular diagrams of **CD1** and **CD2** were generated using ORTEP-3.[23] The data refinement was carried out by the Bruker APEX II software package with SHELXT program.[24]

4.3. DFT calculation details

The optimized geometrical structures, the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) energies of naphthalene, **CD1**, pyrene, and **CD2** were estimated by the DFT calculations (B3LYP/6-31G(d) level of theory) using Spartan '08 for Windows (Wavefunction, Inc., Irvine, CA, USA).[25]

4.4. Materials

1,4-Bis(dimethylhydroxysilyl)naphthalene (**M1**)[15] and 1,6-bis (dimethylhydroxysilyl)pyrene (**M2**)[16] were prepared by the method reported earlier. 7,7,8,8-Tetracyanoquinodimethane (KANTO KAGAKU) was recrystallized from acetonitrile. 1,1,3,3-Tetramethylguanidinium 2-ethylhexanoate was obtained from the equimolar mixture of 1,1,3,3-tetramethylguanidine and 2-ethylhexanoic acid (Tokyo Kasei Kogyo Co., Inc.). Toluene and benzene (Wako Pure Chemical Industries, Ltd.) were used after distillation over sodium. The purity of all synthesized compounds were confirmed to be over 99% from GC analysis.

4.5. Synthesis of siloxane-bridged cyclic dimer containing naphthalene moieties (CD1)

Under a dry argon atmosphere, 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate (0.02 g) was added to a solution of **M1** (2.51 g, 9.10 mmol) in dry benzene (400 mL), and the reaction mixture was refluxed for 18 h with stirring. The reaction mixture was cooled at room temperature to generate a white precipitate. The precipitate was collected by filtration to afford **CD1** as white powder with the yield of 37.8% (0.89 g, 1.72 mmol). Mp: >250 °C (sublimation). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.89 (d, J=3.2 Hz, 4H, naphthylene protons), 7.35 (d, J=3.2 Hz, 4H, naphthylene protons), 6.65 (d, J=3.2 Hz, 4H, naphthylene protons), 0.59 (s, 12H, $-Si(CH_3)_2-$), 0.54 (s, 12H, $-Si(CH_3)_2-$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 136.9 (naphthylene carbon), 134.9 (naphthylene carbon), 131.7 (naphthylene carbon), 129.4 (naphthylene carbon), 124.3 (naphthylene carbon), −3.4 ($-Si(CH_3)_2-$), 0.6 ($-Si(CH_3)_2-$). IR (KBr, cm^{-1}): 1052 (Si–O–Si). Mass (EI, m/z, intensity): 516 (M^+, 9.5%), 243 ($M^+-[Si(CH_3)_2C_{10}H_6Si(CH_3)_2O+CH_3]$, 100%). Anal. Calcd for $C_{28}H_{36}O_2Si_4$: C, 65.06; H, 7.02. Found: C, 65.08; H, 7.14.

4.6. Synthesis of siloxane-bridged cyclic dimer containing pyrene moieties (CD2)

Under a dry argon atmosphere, 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate (0.02 g) was added to a solution of **M2** (3.50 g, 10.0 mmol) in dry toluene (500 mL), and the reaction mixture was refluxed for 24 h with stirring. The reaction mixture was washed with ammonium chloride aqueous solution, dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography eluted with hexane/chloroform (Vol ratio 1:1, R_f value is 0.90). The collected fraction was concentrated under reduced pressure. The residue was recrystallized from benzene to afford **CD2** as yellow crystals with the yield of 44.6% (1.48 g, 2.23 mmol). Mp: 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.93 (d, J=7.6 Hz, 4H, pyrenyl protons), 7.59 (d, J=7.6 Hz, 4H, pyrenyl protons), 7.32 (d, J=9.0 Hz, 4H, pyrenyl protons), 6.93 (d, J=9.0 Hz, 4H, pyrenyl protons), 0.79 (s, 12H, $-Si(CH_3)_2-$), 0.57 (s, 12H, $-Si(CH_3)_2-$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 134.8 (pyrenyl carbon), 133.6 (pyrenyl carbon), 131.4 (pyrenyl carbon), 130.8 (pyrenyl carbon), 127.6 (pyrenyl carbon), 126.3 (pyrenyl carbon), 123.0 (pyrenyl carbon), 122.1 (pyrenyl carbon), 3.52 ($-Si(CH_3)-$), 1.52 ($-Si(CH_3)-$). IR (KBr, cm^{-1}): 1071 (Si–O–Si). Mass (EI, m/z, intensity): 664 (M^+, 100%). Anal. Calcd for $C_{40}H_{40}O_2Si_4$: C, 72.24; H, 6.06. Found: C, 72.29; H, 6.09.

Acknowledgements

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Supplementary data

CCDC 783502 and 783503 contain the supplementary crystallographic data for compounds **CD1** and **CD2**, respectively. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version doi:10.1016/j.tet.2010.08.010.

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