JOC The Journal of Organic Chemistry

Article

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Synthesis and Electronic and Photophysical Properties of [2.2]- and [3.3]Paracyclophane-Based Donor−Donor′−Acceptor Triads¶

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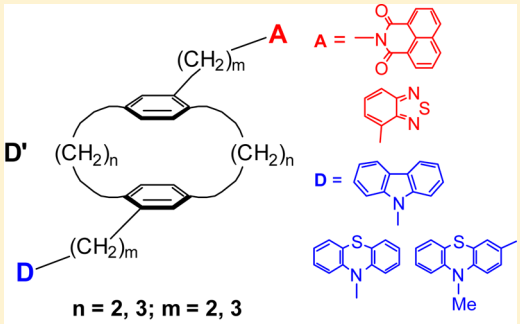
Supporting Information

ABSTRACT: Three types of the donor(D)−donor′(D′)−acceptor(A) triads **1**−**6** with different D−A combinations, carbazole (Cz, D)-[*n.n*]PCP(D′)-1,8-naphthalimide (NI, A) (**1**-**3**), 10*H*-phenothiazine (PTZ, D)-[*n.n*]PCP(D′)-NI(A) (**4**, **5**), and 10-methyl-10*H*-phenothiazine (Me-PTZ, D)-[2.2]PCP-2,1,3-benzothiadiazole (BTD, A) **6**, were synthesized for the elucidation of their photophysical properties. The absorption spectra and electrochemical properties indicated that the chromophores (D, D′, and A) do not interact with each other in the ground state. Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1** and Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2** show an exciplex emission between the PCP and NI moieties in cyclohexane and the intensity of the band is much higher in **2** than in **1**, whereas Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3** does not show any exciplex emission in cyclohexane. These results indicated that the combination of [3.3]PCP and a trimethylene chain is preferable for the exciplex formation. PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4** shows a broad band at 519 nm in cyclohexane, which is associated with the formation of the exterplex band among the NI, [2.2]PCP, and PTZ moieties, while PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5** does not show the band. Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6** shows a broad fluorescence band due to both the BTD and PTZ moieties in cyclohexane. In CH_3CN, the fluorescence spectra of **1**−**6** suggest the presence of a photoinduced charge separation process. The study of the photoinduced charge separation process will be soon reported elsewhere.



[2.2]- and [3.3]Paracyclophane-based donor(D)-donor'(D')-acceptor(A) triads

1. INTRODUCTION

Molecular wires have been intensively studied as an electron and/or hole conducting material.[1,2] The molecular wire as a donor (D)−bridge (B)−acceptor (A) (D−B−A) system has served as a suitable model compound for the elucidation of the electron and/or hole transfer in molecular arrays. Molecular wires are mainly divided into two types, a linear π-conjugated array[3−8] and a π-stack array.[9,10] DNA has been most intensively studied as a model compound for the π-stack type molecular wires. In DNA, a charge transport mechanism and the multistep hopping mechanism have been proposed.[9] Multilayered [2.2]- and [3.3]paracyclophanes (PCPs) have the potential to be a reference of the DNA base pairs as the bridge because the transannular distances of the benzene rings (ca. 3.0−3.3 Å)[11] are similar to those (ca. 3.4 Å) of the base pairs of the double-strand structure of DNA. In addition, efficient charge delocalization over the [3.3]PCPs was observed in the radical cation species of the two- to four-layered [3.3]PCPs based on a pulse radiolysis study.[12] A limited number of the D-B-A systems containing PCPs as a bridge has already been reported.[13,14]

As the first report of our continued efforts to elucidate the properties of the multilayered [2.2]- and [3.3]PCP-based molecular wires with acceptor and donor moieties at the terminals, we reported the syntheses and photophysical properties of the two- and three-layered [3.3]PCP-based D−A systems, in which an external benzene ring of the two- and three-layered [3.3]PCPs is replaced with 2,1,3-benzothiadizole (BTD) as an acceptor.[1a] In both D−A systems, the charge transfer (CT) absorption bands appeared in the longest wavelength region, and the broad fluorescence bands were attributed to the intramolecular exciplex emission. Their redox properties also support the strong electronic interaction between D and A in the ground state. In order to decrease the magnitude of the electronic interaction between D and A in the ground state, we designed a way to connect the D and A moieties at the terminals of the multilayered [2.2]- and [3.3]PCPs, respectively, by single oligomethylene spacers. Thus, we planned to synthesize a series

Received: September 3, 2014
Published: October 31, 2014

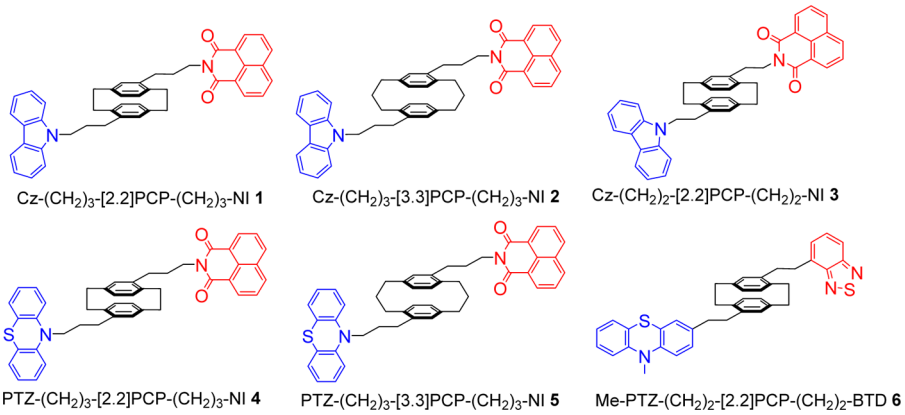
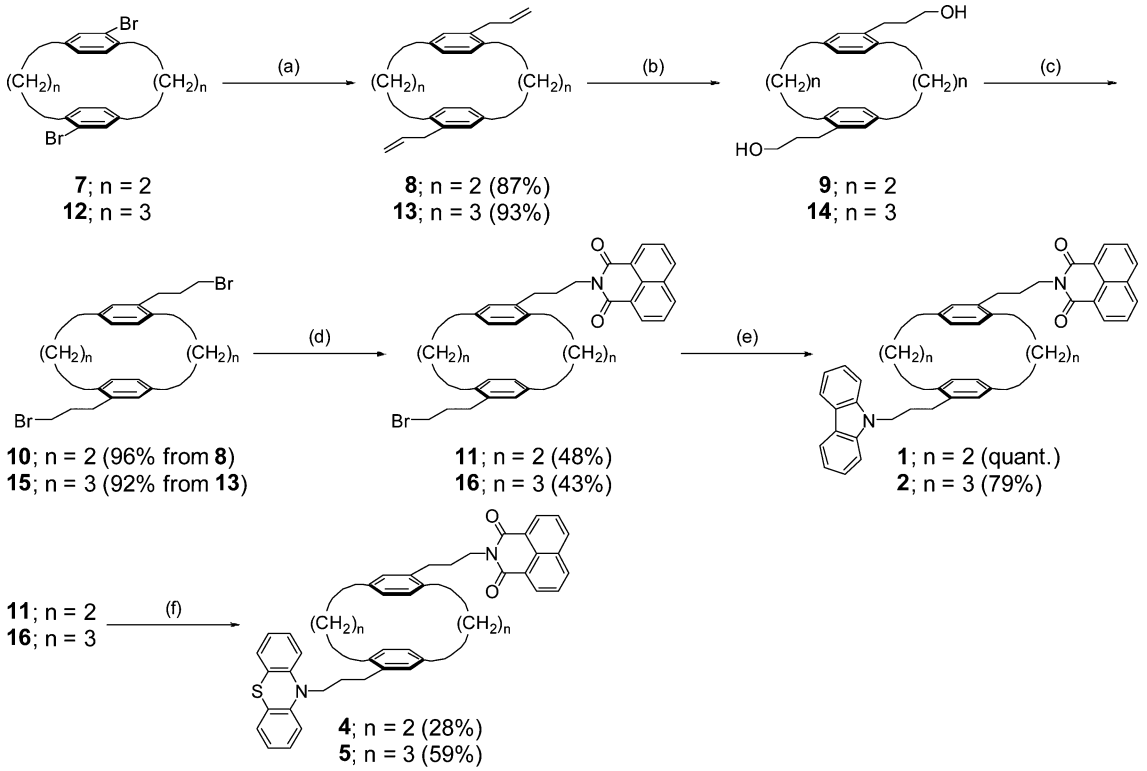


Figure 1. Synthesized D−D′−A triads **1**−**6** containing the [2.2]- or [3.3]PCP moiety as the bridge with electron donating ability (D′).

Scheme 1. Syntheses of Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI 1 and Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI 2 as well as PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI 4 and PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI 5[a]



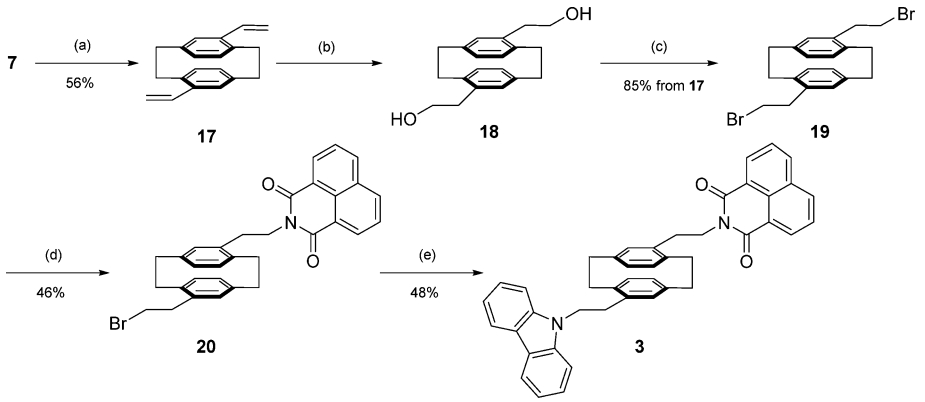
[a]Reagents and conditions: (a) allylSn^{n}Bu$_3$, Pd(PPh$_3$)$_4$, DMF, 100 °C, 1 d; (b) (1) 9-BBN/THF, 40 °C, 3 h, (2) 2 M NaOH aq., 30% H_2O_2 aq., rt, overnight; (c) CBr_4, PPh_3, CH_2Cl_2, rt, 3 h; (d) 1,8-naphthalimide, Cs_2CO_3, DMF, rt, overnight; (e) carbazole, *n*-Bu_4NBr, toluene, 2 M NaOH aq., reflux, 2 d; (f) 10*H*-phenothiazine, *t*-BuOK, DMF, rt, overnight.

of D-D′(multilayered PCP)-A systems for the study of the dependence of the rate of charge transport on the D−A distance, i.e., how a charge is transported through the benzene rings in the multilayered PCP in the D−D′−A system. As the first step along this line, we now report the syntheses, and electronic and photophysical properties of the simplest triads in this series with two-layered PCPs as the D′. The triads, which can be grouped into three types of the D−A combinations, carbazole (Cz, D)[15]-$(CH_2)_m$-[*n*.*n*]PCP(D′)-$(CH_2)_m$-1,8-naphthalimide (NI, A)[15a,d,16] (**1**: n = 2, m = 3; **2**, n = 3, m = 3; **3**, n = 2, m = 2), 10*H*-phenothiazine (PTZ, D)[17]-$(CH_2)_m$-[*n*.*n*]PCP (D′)-$(CH_2)_m$-NI(A) (**4**: n = 2, m = 3; **5**: n = 3, m = 3), as well as 10-methyl-10*H*-phenothiazine (Me-PTZ, D)-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-2,1,3-benzothiadiazole (BTD, A) **6** (Figure 1).

On the basis of the detailed study of the absorption, fluorescence, and transient absorption spectra of the triads **1**−**6** along with their reference compounds, the dependence of the electronic interaction between the A and D′ as well as D′and D moieties in the photoexcited state on the length of the oligomethylene linkers and the transannular distance of the benzene rings should be elucidated. As a result, the photophysical properties of the triads **1**−**6**, such as the charge separation process, should become clear by the analysis of the femto-second transient absorption spectra of the triads and reference compounds. In this paper, we report the syntheses, redox

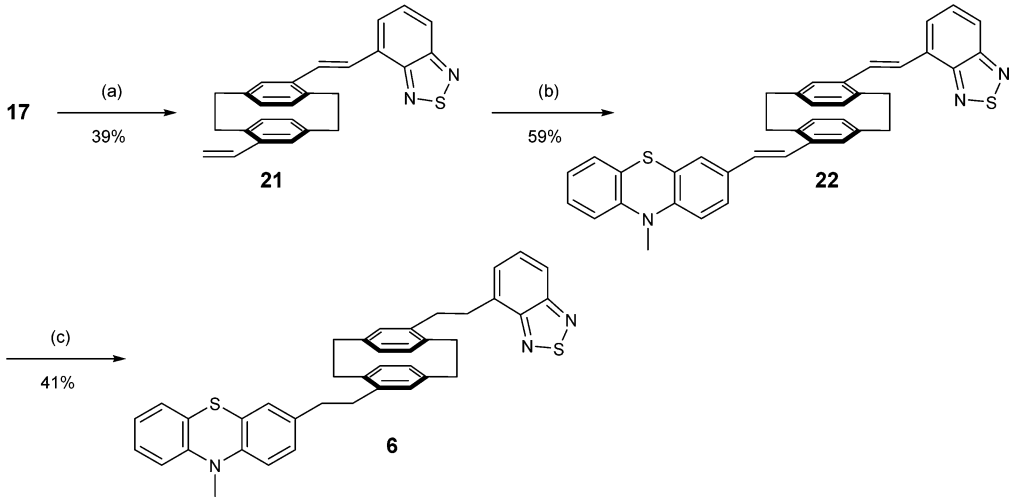
dx.doi.org/10.1021/jo5020273 | J. Org. Chem. 2014, 79, 11440−11453

Scheme 2. Synthesis of Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI 3[a]



[a]Reagents and conditions: (a) vinylSn^{n}Bu$_3$, Pd(PPh$_3$)$_4$, toluene, 100 °C, 1 d; (b) (1) 9-BBN/THF, 60 °C, overnight, (2) 2 M NaOH aq., 30% H_2O_2 aq., rt, 6 h; (c) CBr_4, PPh_3, CH_2Cl_2, rt, 3 h; (d) 1,8-naphthalimide, Cs_2CO_3, DMF, rt, overnight; (e) carbazole, *n*-Bu_4NBr, toluene, 2 M NaOH aq., reflux, 2 d.

Scheme 3. Synthesis of Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD 6[a]



[a]Reagents and conditions: (a) 4-bromo-BTD, Pd(OAc)$_2$, *n*-Bu_4NBr, K_2CO_3, DMF, 100 °C, 2 d; (b) 3-bromo-Me-PTZ, Pd(dppf)Cl_2·CH_2Cl_2, *n*-Bu_4NBr, K_2CO_3, DMF, 100 °C 1 d; (c) NH_2NH_2·H_2O, diethylene glycol, 100 °C, 20 h.

properties, and absorption and fluorescence spectra of the triads **1**–**6**, while the detailed discussion on the transient absorption spectral study will be reported elsewhere.

2. RESULTS AND DISCUSSION

Synthesis. The [2.2]PCP-based triad with carbazole (Cz) as a donor and 1,8-naphthalimide (NI) as an acceptor with trimethylene linkers, Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1**, was synthesized from 4,12-dibromo[2.2]PCP **7**, which was prepared from [2.2]PCP according to the reported procedures[18] in 5 steps (Scheme 1). The pseudo-*para*-substituted dibromide **7** was reacted with allyltributyltin in the presence of Pd(PPh$_3$)$_4$ in DMF at 100 °C to give 4,12-diallyl[2.2]PCP **8** (87%), which was converted into the diol **9** by hydroboration with 9-borabicyclo[3.3.1]nonane (9-BBN) in THF, followed by oxidation with 30% aqueous H_2O_2 under basic conditions. The diol **9** was brominated with CBr_4 and PPh_3 in CH_2Cl_2 at room temperature to give the dibromide **10** (96% from **8**). The donor and acceptor moieties were introduced into the [2.2]PCP skeleton in a stepwise manner. *N*-alkylation of the NI moiety with the dibromide **10** in the presence of Cs_2CO_3 in DMF at room temperature provided Br$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **11** (48%). Further *N*-alkylation of the Cz moiety by the bromide **11** in the presence of *n*-Bu_4NBr as a phase-transfer catalyst in toluene and 2 M aqueous NaOH at reflux afforded the desired triad **1** (quant.). The [3.3]PCP-based triad, Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2**, was synthesized starting from 4,14-dibromo[3.3]PCP **12**[19] by a similar series of reactions reported for the synthesis of **1**. The introduction of the PTZ moiety as a donor into the NI-substituted [2.2]PCP derivative was achieved by the reaction of the PTZ anion generated by *t*-BuOK in DMF at room temperature with the bromide **11** to give the triad, PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4** (28%). A similar *N*-alkylation of the PTZ moiety with the bromide **16** afforded PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5** (59%).

The triad with the dimethylene linkers, Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3**, was synthesized from 4,12-divinyl[2.2]PCP **17**,[14b] which was derived from 4,12-dibromo[2.2]PCP **7** by the reaction with vinyltributyltin in the presence of Pd(PPh$_4$)$_4$ in toluene at 100 °C (56%). Hydroboration of **17**, followed by bromination of the resultant diol **18** afforded the dibromide **19**. Stepwise introduction of the NI and Cz moieties into the [2.2]PCP

dx.doi.org/10.1021/jo5020273 | J. Org. Chem. 2014, 79, 11440–11453

Table 1. Redox Potentials (V vs Fc/Fc^+) and HOMO and LUMO Energies of 1−6, Me-Cz, Me-PTZ, Me-NI, BTD, [2.2]PCP, and [3.3]PCP in CH_3CN Containing 0.1 M n-Bu_4PF_6

	$E^{red}(I)$/V	$E^{ox1}(I)$/V	$E^{ox2}(I)$/V	HOMO[c]/eV	LUMO[d]/eV	E_{gap}/eV
Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1**	−1.75[a]	+0.77[b]		−5.57	−3.05	2.52
Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2**	−1.75[a]	+0.76[b]		−5.56	−3.05	2.51
Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3**	−1.74[a]	+0.74[b]		−5.54	−3.06	2.48
PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4**	−1.71[b]	+0.26[b]	+0.90[b]	−5.06	−3.09	1.97
PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5**	−1.73[b]	+0.26[b]	+0.87[b]	−5.06	−3.07	1.99
Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6**	−1.93[a]	+0.25[a]	+0.84[b]	−5.05	−2.87	2.18
Me-Cz		+0.74[b]		−5.54		
Me-PTZ		+0.30[a]	+0.91[b]	−5.10		
Me-NI	−1.73[a]				−3.07	
BTD	−1.89[a]				−2.91	
[2.2]PCP		+1.09[b]		−5.89		
[3.3]PCP		+0.98[b]	+1.30[b]	−5.78		

[a]The potential $E(I)$ was determined by CV at the potential scan rate of 100 mV s^{-1}. [b]The potential $E(I)$ was determined by DPV at the potential scan rate of 20 mV s^{-1}. [c]HOMO = −4.8 − $E^{ox}(I)$. [d]LUMO = −4.8 − $E^{red}_{1/2}(I)$.

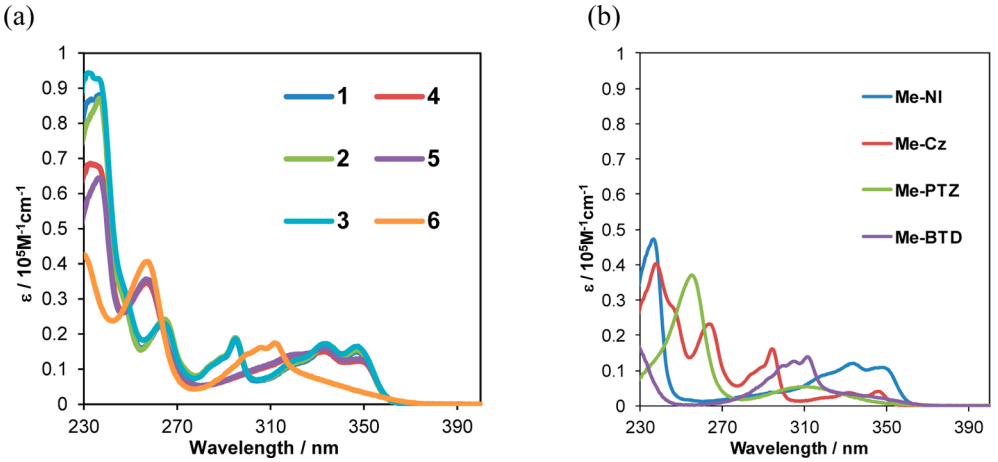


Figure 2. (a) Absorption spectra of Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1** (blue), Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2** (green), Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3** (light blue), PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4** (red), PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5** (purple), and Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6** (orange) in CH_2Cl_2. (b) Absorption spectra of Me-NI (blue), Me-Cz (red), Me-PTZ (green), and Me-BTD (purple) in CH_2Cl_2.

skeleton by the successive *N*-alkylation reactions afforded the desired triad **3** (Scheme 2).

The synthesis of the triad, Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6**, was achieved from 4,12-divinyl[2.2]PCP **17** according to the procedures shown in Scheme 3. An acceptor moiety, BTD, and a donor moiety, Me-PTZ, were introduced into the [2.2]PCP skeleton by the Heck coupling reaction in a stepwise manner. The divinyl compound **17** was reacted with 4-bromo-2,1,3-benzothiadiazole in the presence of $Pd(OAc)_2$, n-Bu_4NBr, and K_2CO_3 in DMF at 100 °C for 2 d to give the BTD-substituted [2.2]PCP **21** (39%), which was further reacted with 3-bromo-10-methyl-10*H*-phenothiazine in the presence of $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$, n-Bu_4NBr, and K_2CO_3 in DMF at 100 °C to afford the BTD- and Me-PTZ-tethered [2.2]PCP **22** (59%). Finally, the olefinic double bonds of **22** were reduced with $NH_2NH_2{\cdot}H_2O$ in diethylene glycol at 100 °C to give the desired **6** as yellow crystals from a mixture of toluene and MeOH (41%).

Electrochemical Properties. For the evaluation of the magnitude of the electronic interaction between the chromophores in the ground state, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of **1**−**6** were measured in CH_3CN containing 0.1 M n-Bu_4NPF_6 vs Fc/Fc^+ along with Me-Cz, Me-PTZ, Me-NI, BTD, [2.2]PCP, and [3.3]PCP as references (Figures S1 and S2). The observed redox potentials and the HOMO and LUMO energies estimated by the redox potentials in CH_3CN are summarized in Table 1. The DFT (B3LYP/6-31G* level) calculations (Gaussian 09)[20] of the HOMO and LUMO orbitals of **1**, **2**, and **3** indicated that their LUMO orbitals are completely localized over the NI moiety, while their HOMO orbitals are mostly localized over the Cz moiety and partially localized over the [2.2]- or [3.3]PCP moieties through the di- and trimethylene linkers. The calculations also showed that the HOMO and LUMO orbitals of **4**, **5**, and **6** are completely localized over the PTZ and NI or BTD moieties, respectively (Figure S3). These results suggest almost no orbital interaction between A and D′ as well as D and D′ in the ground state.

Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1** shows one reversible reduction process ($E^{red}(I)$: −1.75 V) and one irreversible oxidation process ($E^{ox}(I)$: +0.77 V), which was determined by DPV, in CH_3CN containing 0.1 M n-Bu_4NPF_6 vs Fc/Fc^+ (Figure S1). Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2** and Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3** also exhibited CV and DPV profiles similar to those of **1** (**2**, $E^{red}(I)$: −1.75 V, $E^{ox}(I)$: +0.76 V; **3**, $E^{red}(I)$: −1.74 V, $E^{ox}(I)$: +0.74 V).[21] The values of the redox potentials are in good agreement with those of the components, Me-NI ($E^{red}(I)$: −1.73 V) and Me-Cz ($E^{ox}(I)$: +0.74 V). PTZ-

dx.doi.org/10.1021/jo5020273 | J. Org. Chem. 2014, 79, 11440−11453

Table 2. Absorption Bands (λ_{max}) and Molar Absorbance of 1−6, Me-NI, Me-Cz, Me-PTZ, and Me-BTD in CH_2Cl_2, CH_3CN, and Cyclohexane

compound	λ_{max}/nm (log ε)		
	CH_2Cl_2	CH_3CN	cyclohexane
Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1**	236 (4.96), 265 (4.36), 295 (4.26), 334 (4.20), 347 (4.18)	230 (4.97), 263 (4.39), 294 (4.29), 332 (4.19), 346 (4.17)	231 (4.99), 236 (4.98), 263 (4.38), 294 (4.41), 330 (4.21), 345 (4.23)
Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2**	237 (4.94), 266 (4.38), 295 (4.28), 334 (4.21), 347 (4.19)	235 (4.90), 262 (4.34), 294 (4.22), 332 (4.17), 346 (4.15)	236 (4.91), 264 (4.30), 294 (4.33), 330 (4.16), 345 (4.17)
Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3**	232 (4.97), 264 (4.36), 295 (4.27), 333 (4.24), 348 (4.22)	230 (4.96), 263 (4.42), 294 (4.32), 331 (4.20), 346 (4.19)	230 (4.92), 261 (4.27), 295 (4.30), 330 (4.17), 345 (4.20)
PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4**	233 (4.84), 257 (4.54), 333 (4.18), 348 (4.09)	231 (4.81), 256 (4.53), 331 (4.16), 343 (4.07)	232 (4.84), 256 (4.54), 326 (4.17), 345 (4.09)
PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5**	237 (4.81), 257 (4.55), 334 (4.20), 348 (4.11)	234, 256, 330, 345[a]	236, 256, 326, 344[a]
Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6**	258 (4.61), 312 (4.24)	256 (4.67), 311 (4.26)	257 (4.71), 311 (4.33)
Me-NI	237 (4.67), 334 (4.08), 348 (4.03)	234 (4.65), 332 (4.05), 343 (4.01)	235 (4.67), 330 (4.03), 344 (4.03)
Me-Cz	238 (4.60), 264 (4.36), 295 (4.20), 332 (3.56), 346 (3.60)	236 (4.64), 262 (4.35), 293 (4.19), 331 (3.54), 345 (3.57)	236 (4.67), 262 (4.32), 293 (4.64), 328 (3.60), 344 (3.74)
Me-PTZ	255 (4.57), 310 (3.73)	255 (4.62), 311 (3.76)	253 (4.60), 309 (3.72)
Me-BTD	305 (4.10), 312 (4.14)	303 (4.06), 310 (4.09)	304 (4.06), 310 (4.09)

[a]Log ε was not determined due to the low solubility.

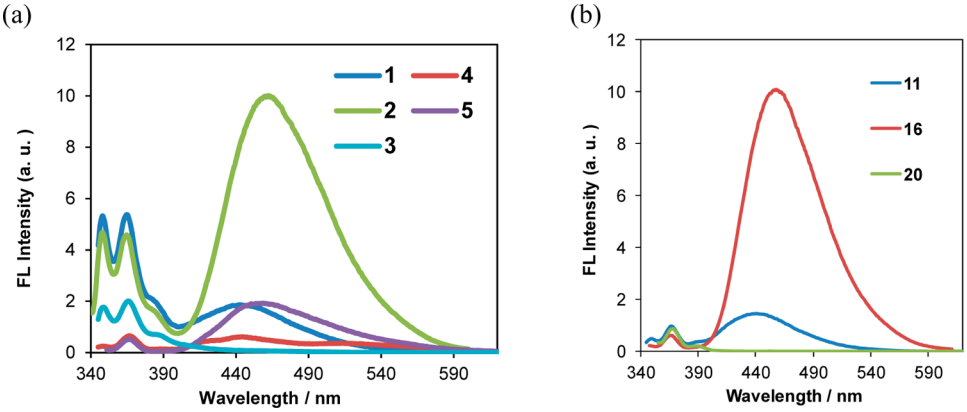


Figure 3. (a) Fluorescence spectra of Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1** (blue), Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2** (green), Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3** (light blue), PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4** (red), PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5** (purple) in cyclohexane (λ_{ex} = 330 nm). (b) Fluorescence spectra of Br$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **11** (blue), Br$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **16** (red), and Br$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **20** (green) in cyclohexane (λ_{ex} = 330 nm).

$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4** and PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5** show one reduction process (**4**, $E^{red}(I)$: −1.71 V; **5**, $E^{red}(I)$: −1.73 V) and two oxidation processes (**4**, $E^{ox}(I)$: +0.26, +0.90 V; **5**, $E^{ox}(I)$: +0.26, +0.87 V), corresponding to the redox potentials of the NI and PTZ (Me-PTZ, $E^{ox}(I)$: +0.30, +0.91 V) moieties, respectively. Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6** shows a reversible one-electron reduction process ($E^{red}(I)$: −1.93 V) and two oxidation processes ($E^{ox}(I)$: +0.25, +0.84 V) in CH_3CN, and their potentials are quite similar to the reduction potential of BTD ($E^{red}(I)$: −1.89 V) and the oxidation potential of Me-PTZ, respectively. These results clearly indicated that the donor and acceptor moieties in each of the compounds do not interact with each other and with the [2.2]- or [3.3]PCP moiety in the ground state. As expected, the connection of the D, D′, and A moieties with di- or trimethylene linkers significantly decreases the magnitude of the electronic interaction between the neighboring chromophores, and this is in sharp contrast to the reduction potential of the BTD moiety incorporated into the [3.3]PCP moiety in the two- and three-layered [3.3]PCP-based D−A diads, in which the BTD moiety shows higher reduction potentials than that of BTD itself due to the effective transannular electronic interaction with the [3.3]PCP moiety.[1a]

Absorption Spectra. The absorption spectra of the D−D′−A triads **1**−**6**, their components, Me-NI, Me-Cz, Me-PTZ, and Me-BTD, as well as related reference compounds were measured in CH_2Cl_2 (Figure 2), and their λ_{max} and molar absorbance are summarized in Table 2. Me-NI shows a broad structured absorption band in the region of ca. 260−360 nm (λ_{max} = 334 and 348 nm) along with a sharp absorption band at 237 nm above 220 nm, while Me-Cz exhibits broad structured absorption bands in the region of ca. 310−350 nm (λ_{max} = 332 and 346 nm) and three sharp absorption bands at 238, 264, and 295 nm (Figure 2b). Me-PTZ shows a sharp band at 255 nm and a broad structureless band at ca. 310 nm above 230 nm, whereas Me-BTD exhibits structured broad bands in the region of 270−320 nm (λ_{max} = ca. 310 nm). The Cz-$(CH_2)_m$-[*n*.*n*]PCP-$(CH_2)_m$-NI triads, **1** (n = 2, m = 3), **2** (n = 3, m = 3), and **3** (n = 2, m = 2), show quite similar absorption bands at 236, 265, and 295 nm as well as in the region of ca. 310−360 nm, which are a superposition of those of the components, Me-Cz and Me-NI. The PTZ-$(CH_2)_3$-[*n*.*n*]PCP-$(CH_2)_3$-NI triads, **4** (n = 2) and **5** (n = 3), also show

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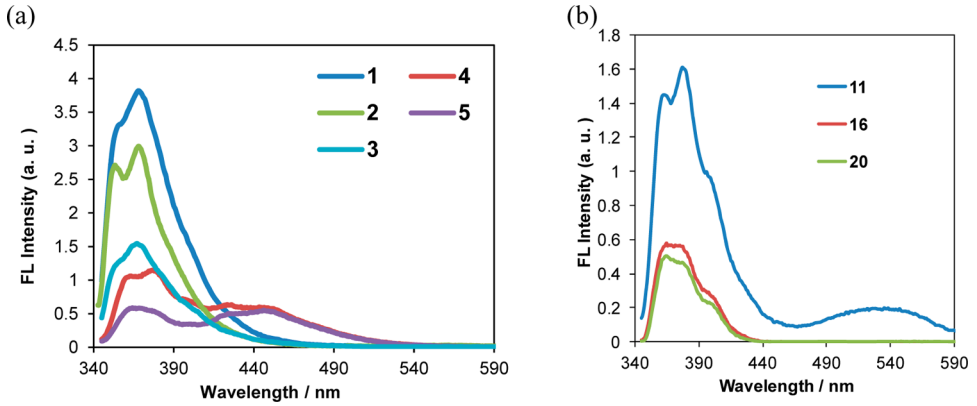
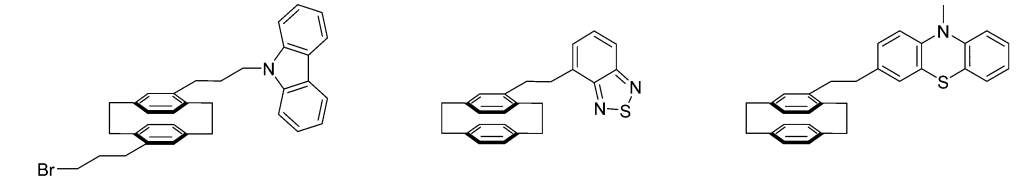


Figure 4. (a) Fluorescence spectra of Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1** (blue), Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2** (green), Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3** (light blue), PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4** (red), PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5** (purple) in CH_3CN (λ_{ex} = 330 nm). (b) Fluorescence spectra of Br-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **11** (blue), Br$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **16** (red), and Br$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **20** (green) in CH_3CN (λ_{ex} = 330 nm).



Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$Br **23** [2.2]PCP-$(CH_2)_2$-BTD **24** Me-PTZ-$(CH_2)_2$-[2.2]PCP **25**

Figure 5. Reference compounds **23**–**25**.

quite similar absorption spectra to each other at 257 nm as a sharp band and at ca. 280–360 nm as a structured broad band, which are a superposition of those of the components, Me-PTZ and Me-NI. Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6** shows a sharp band at 258 nm and a structured broad band at ca. 310 nm, and the spectrum is the simple superposition of those of the Me-PTZ and Me-BTD. These data clearly indicated that the chromophores (D, D′, A) do not interact with each other in the ground state, as was supported by the redox potentials. No significant solvent effect was observed in the absorption spectra of **1**–**6** in cyclohexane, CH_2Cl_2, and CH_3CN, and no CT band was observed for any of the evaluated compounds (Figures S4 and S5). Thus, we confirmed that the magnitude of the electronic interaction among the chromophores can be significantly reduced in the ground state by connecting the chromophores with a single oligomethylene chain.

Fluorescence Spectra. The fluorescence spectra of the D–D′–A triads **1**–**5** and their components, Me-NI, Me-Cz, and Me-PTZ, were measured at 330 nm as the excited wavelength in diluted cyclohexane (Figures 3a and S7), CH_2Cl_2 (Figure S8), and CH_3CN (Figures 4a and S9) solutions ($\leq 10^{-5}$ M) to eliminate the intermolecular interaction. The fluorescence spectra of the reference compounds, such as Br$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **11**, Br$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **16**, and Br$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **20** (Figures 3b, 4b, and Figure S8b), as well as Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$Br **23** (Figures 5, S7c, S8e, and S9c) were also measured under the same conditions. All the data are summarized in Table 3.

Me-NI exhibits structured low intensity fluorescence bands at 349, 366, and 387 nm (Φ_f 0.005), while Me-Cz shows significantly high intensity fluorescence bands at 345 and 362 nm (Φ_f 0.68) in cyclohexane (Figure S7a). Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1** shows not only structured fluorescence bands at 350 and 367 nm, but also a broad band at 441 nm (Φ_f 0.009) in cyclohexane. The latter broad band can be assigned as the fluorescence band due to the exciplex formation between the NI and [2.2]PCP moieties since Br$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **11** also shows a similar broad band at 441 nm (Φ_f 0.009) in cyclohexane (Figure 3b). The bands in the shorter wavelength region are assigned as those due to the Cz and NI moieties, but their intensities are significantly decreased compared to those of Me-Cz and Me-NI. When the Cz moiety of **1** is selectively excited at 262 nm in cyclohexane, the fluorescence band appears at 443 nm due to the exciplex formation between the NI and [2.2]PCP moieties (Figure S10), and the excitation spectrum at 443 nm is similar to the absorption spectrum of Me-Cz (Figure S11). In addition, the fluorescence spectrum of Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$Br **23** is quite similar to that of Me-Cz and the quantum yield is slightly decreased (λ_{max} = 348 and 364 nm, Φ_f 0.57) in cyclohexane (Figure S7c). These results indicated that the Cz moiety and the [2.2]PCP moiety do not interact with each other in the excited state and the intramolecular energy transfer from the Cz moiety in the excited state to the NI moiety is expected in **1**. In sharp contrast, the triad **1** shows only a broad structured fluorescence band at 354 and 369 nm in CH_2Cl_2 (Figure S8a) and at 368 nm in CH_3CN (Figure 4a) (Φ_f 0.006 in CH_2Cl_2, 0.004 in CH_3CN). The exciplex emission is quenched in CH_2Cl_2 and CH_3CN, suggesting the presence of a photoinduced charge separated state, $Cz^{\bullet+}$-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-$NI^{\bullet-}$.

The fluorescence spectra of Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2** in cyclohexane and CH_3CN are similar to those of **1**, suggesting the presence of an intramolecular energy transfer from the Cz moiety in the excited state to the NI moiety in cyclohexane and a photoinduced charge separation process in CH_3CN. Interestingly, **2** shows a much higher intensity band due to the exciplex formation at 465 nm (Φ_f 0.050) in cyclohexane and at 542 nm

dx.doi.org/10.1021/jo5020273 | J. Org. Chem. 2014, 79, 11440–11453

Table 3. Fluorescence Data of the Triads 1−5, 11, 16, 20, 23, 6, 24, 25, Me-NI, Me-Cz, Me-PTZ, and Me-BTD in Cyclohexane, CH_2Cl_2, and CH_3CN

compound	λ_{max}/nm (Φ_f[a])		
	cyclohexane	CH_2Cl_2	CH_3CN
Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **1**[b]	350, 367, 441 (0.009)	354, 369, 560 (0.006)	368 (0.004)
Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **2**[b]	348, 365, 465 (0.050)	353, 368, 542 (0.012)	353, 368 (0.005)
Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3**[b]	349, 366 (0.004)	354, 368, 544 (0.003)	367 (0.003)
PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4**[b]	366, 448, 519 (0.008)	377, 449 (0.004)	379, 443 (0.005)
PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5**[b]	459 (0.015)	379, 447 (0.004)	364, 446 (0.005)
Br$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **11**[b]	350, 367, 441 (0.006)	362, 379, 504 (0.031)	363, 377, 535 (0.004)
Br$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **16**[b]	458 (0.051)	375, 534 (0.019)	365 (0.004)
Br$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **20**[b]	349, 368 (0.003)	370, 377, 540 (0.004)	364 (0.003)
Cz-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$Br **23**[b]	348, 364 (0.57)	352, 369 (0.31)	352, 368 (0.53)
Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6**[c]	407 (0.012)	450 (0.004)	450 (0.004)
[2.2]PCP-$(CH_2)_2$-BTD **24**[c]	394 (0.014)	499 (0.006)	537 (0.004)
Me-PTZ-$(CH_2)_2$-[2.2]PCP **25**[c]	445 (0.010)	451 (0.011)	450 (0.011)
Me-NI[b]	349, 366, 387 (0.005)	361, 379 (0.040)	361, 377 (0.029)
Me-Cz[b]	345, 362 (0.68)	351, 368 (0.34)	352, 368 (0.61)
Me-PTZ	442[b]; 444 (0.009)[c]	448[b]; 449 (0.010)[c]	445[b]; 447 (0.011)[c]
Me-BTD[c]	389 (0.013)	409 (0.022)	414 (0.027)

[a]Absolute quantum yields. [b]λ_{ex} = 330 nm. [c]λ_{ex} = 312 nm.

(Φ_f 0.012) in CH_2Cl_2 (Figure S8a) than that of the [2.2]PCP-based triad **1**, and this indicated that the [3.3]PCP moiety has a stronger tendency to form the exciplex with the NI moiety than the [2.2]PCP moiety, probably because of the stronger electron donating ability of the former than the latter (Table 1).[22] The fluorescence spectrum of Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3** is solvent dependent. In cyclohexane, **3** shows only broad structured bands at 349 and 366 nm (Φ_f 0.004) and the band due to the exciplex emission cannot be observed, similar to the fluorescence spectrum of Br$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **20** in cyclohexane, while **3** shows the exciplex band at 499 nm in toluene (Figure S12).[23] These results clearly indicated that a trimethylene chain is more favorable as a linker for the formation of the exciplex than a dimethylene chain, as suggested by a statistical rule known as Hirayama's n = 3 rule.[24] Similar to the cases of **1** and **2**, the photoinduced charge separation process is expected for **3** in CH_3CN.

As a reference experiment, we examined the intermolecular exciplex formation between the PCP and NI moieties in cyclohexane. In a mixture of [3.3]PCP (10^{-2} M) and Me-NI (10^{-4} M) in cyclohexane, the intermolecular exciplex band was clearly observed, while its intensity at 440−540 nm was significantly decreased in the solution of a mixture of [3.3]PCP (10^{-3} M) and Me-NI (10^{-4} M) (Figure S13). Similar weak band due to the intermolecular exciplex was observed in a mixture of [2.2]PCP (10^{-3} M) and Me-NI (10^{-4} M), while the clear exciplex band was not observed because of the limited solubility of [2.2]PCP in cyclohexane.

The triad with a different D−A combination, PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4**, shows two structured fluorescence bands at 366 and 448 nm due to the NI and PTZ moieties, respectively, and a broad band in a much longer wavelength region (519 nm, Φ_f 0.008) than that of the exciplex between the NI and [2.2]PCP moieties in cyclohexane. The band at 519 nm is associated with the formation of the exterplex (termolecular exciplex)[25] among the NI, [2.2]PCP, and PTZ moieties because the excitation spectrum of **4** at 520 nm is a superposition of the absorption spectra of Me-PTZ and Me-NI in cyclohexane (Figure S14). The formation of the intermolecular exterplex among Me-NI, [2.2]PCP, and Me-PTZ could not be examined because of the limited solubility of [2.2]PCP and Me-NI in cyclohexane. A more detailed study is required for the assignment of this band.

In CH_2Cl_2 and CH_3CN, **4** shows two structured fluorescence bands at 377 and 449 nm (Φ_f 0.004) in CH_2Cl_2 as well as at 379 and 443 nm (Φ_f 0.005) in CH_3CN due to the NI and PTZ moieties, respectively, suggesting the presence of a photoinduced charge separation process in these solvents. PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5** also shows a broad fluorescence band at 459 nm (Φ_f 0.015) in cyclohexane, which is assigned as the overlap of the bands due to the PTZ moiety and the exciplex emission between the NI and [3.3]PCP moieties, but the band due to the exterplex emission is not observed. The triads **4** and **5** show only broad structured bands due to the NI and PTZ moieties, respectively, in CH_3CN (**4**: 379 and 443 nm, Φ_f 0.005; **5**: 364 and 446 nm, Φ_f 0.005), suggesting a photoinduced charge separation process.

The fluorescence spectra of Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6** and its reference compounds, such as Me-BTD, Me-PTZ, [2.2]PCP-$(CH_2)_2$-BTD **24**, and Me-PTZ-$(CH_2)_2$-[2.2]PCP **25** were measured in cyclohexane (Figure S7d), CH_2Cl_2 (Figure S8f) and CH_3CN (Figure S9d) using 312 nm light for excitation and a 10^{-5} M sample concentration to eliminate any intermolecular interaction. The triad **6** shows a broad fluorescence band due to both the BTD and PTZ moieties in cyclohexane (Φ_f 0.012), whereas **6** exhibits a broad and low intensity fluorescence band at 450 nm (Φ_f 0.004) in CH_2Cl_2 and CH_3CN, and the λ_{max} and its intensity are similar to those of Me-PTZ due to the quenching of the fluorescence band by the BTD moiety. This indicated a photoinduced charge separation process. [2.2]PCP-$(CH_2)_2$-BTD **24** shows a fluorescence band similar to Me-BTD in cyclohexane (394 nm, Φ_f 0.014), whereas the exciplex emission between the BTD and [2.2]PCP moieties is observed in CH_2Cl_2 (Scheme S8f) and CH_3CN (Scheme S9d). The fluorescence spectrum and its quantum yield of Me-PTZ-$(CH_2)_2$-[2.2]PCP **25** are similar to those of Me-PTZ in cyclohexane, CH_2Cl_2, and CH_3CN, indicating that the PTZ moiety in the excited state cannot interact with the [2.2]PCP moiety in **25** and **6**.

dx.doi.org/10.1021/jo5020273 | J. Org. Chem. 2014, 79, 11440−11453

3. CONCLUSIONS

The new D−D′−A triads with three types of the D−A combinations, Cz-$(CH_2)_m$-[*n.n*]PCP-$(CH_2)_m$-NI (**1**: *n* = 2, *m* = 3; **2**, *n* = 3, *m* = 3; **3**, *n* = 2, *m* = 2), PTZ-$(CH_2)_m$-[*n.n*]PCP-$(CH_2)_m$-NI (**4**: *n* = 2, *m* = 3; **5**: *n* = 3, *m* = 3), and Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6** were successfully synthesized. The redox potentials of **1**−**6** in CH_3CN are in good agreement with those of the donor and acceptor components. The absorption spectra of **1**−**6** show spectra similar to a superposition of those of the components in cyclohexane, CH_2Cl_2, and CH_3CN. No significant solvent effect was observed in the absorption spectra of **1**−**6** in cyclohexane, CH_2Cl_2, and CH_3CN, and no CT band was observed for any of the evaluated compounds. These data clearly indicate that the chromophores do not interact with each other in the ground state, as we expected at the start of this study.

All the fluorescence spectra of **1**−**6** are quenched in CH_3CN, suggesting the presence of a photoinduced charge separation process. In the same D−A combination, Cz-$(CH_2)_3$-[3.3]-PCP-$(CH_2)_3$-NI **2** shows a more intensive exciplex emission band than in Cz-$(CH_2)_3$-[2.2]-PCP-$(CH_2)_3$-NI **1** in cyclohexane, while Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3** do not show any exciplex emission in cyclohexane. These results suggest that a combination of [3.3]PCP as D′ and a trimethylene chain as a linker is more suitable for the formation of the exciplex than that of [2.2]PCP and a dimethylene chain, probably because of higher electron donating ability of [3.3]PCP.[22]

In the triads with the PTZ (D) and NI (A) combination, PTZ-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$-NI **4** show a broad fluorescence band at 519 nm in cyclohexane, which may be associated with the exterplex among the NI, [2.2]PCP, and PTZ moieties, while PTZ-$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **5** does not show this type of band, but shows a broad fluorescence band, which may be assigned as the superposition of the bands due to the exciplex formation between the NI and PCP moieties and the PTZ moiety in cyclohexane. The triads **4** and **5** show only broad structured bands due to the NI and PTZ moieties in CH_3CN, suggesting a photoinduced charge separation process. Me-PTZ-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-BTD **6** shows a broad fluorescence band due to both the BTD and PTZ moieties in cyclohexane, whereas **6** exhibits a broad and low intensity fluorescence band due to the PTZ moiety in CH_2Cl_2 and CH_3CN, indicating a photoinduced charge separation process.

Thus, the electronic interaction between the PCP and acceptor moieties can be observed as the exciplex formation in cyclohexane. The formation of the exciplex is more significant in the triad with a [3.3]PCP moiety as D′ and a trimethylene chain as a linker. In all the triads **1**−**6**, the quenching of the fluorescence band is observed in CH_3CN, which suggests the presence of the charge separated state, probably starting from D-$(CH_2)_m$-[*n.n*]PCP-$(CH_2)_m$-A* to $D^{\bullet+}$-$(CH_2)_m$-[*n.n*]PCP-$(CH_2)_m$-$A^{\bullet-}$ via D-$(CH_2)_m$-[*n.n*]$PCP^{\bullet+}$-$(CH_2)_m$-$A^{\bullet-}$. Our collaborators have studied the photoinduced charge separation processes of the triads **1**−**6** and the reference compounds in detail using the transient absorption spectra, the result of which will be soon reported elsewhere. Syntheses of the next triads with triple-layered [2.2]- and [3.3]PCPs are also in progress.

4. EXPERIMENTAL SECTION

4,12-Diallyl[2.2]paracyclophane 8. A mixture of 4,12-dibromo[2.2]PCP **7** (1.83 g, 5.00 mmol), allyltributyltin (7.28 g, 22.0 mmol), $Pd(PPh_3)_4$ (0.92 g, 0.80 mmol), and DMF (180 mL) was stirred at 100 °C for 36 h under an Ar atmosphere. The solvent was removed under reduced pressure, and the residue was purified by SiO_2 column chromatography containing 10 wt % K_2CO_3 (hexane/CH_2Cl_2, 5/1, R_f = 0.27). The eluate was evaporated under reduced pressure and the solid was washed with MeOH to give 4,12-diallyl[2.2]PCP **8** as colorless powder (1.25 g, 87%): mp 106−108 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.77 (m, 2H), 3.01 (m, 4H), 3.09 (m, 2H), 3.32 (m, 2H), 3.38 (m, 2H), 5.04 (m, 4 H), 5.85 (m, 2H), 6.13 (s, 1H), 6.31 (d, *J* = 7.8 Hz, 2H), 6.64 (dd, *J* = 7.8, 1.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.8, 33.5, 38.8, 115.6, 126.7, 133.6, 134.3, 136.8, 137.6, 139.2, 139.4; HRMS (FAB-TOF) *m*/*z* calcd. for $C_{22}H_{24}$ 288.1878 [M^+], found 288.1881. Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.42; H, 8.42.

4,12-Bis(3-bromopropyl)[2.2]paracyclophane 10. 4,12-Diallyl-[2.2]PCP **8** (0.29 g, 1.00 mmol) was added to a 0.5 M THF solution of 9-BBN (8.0 mL, 4.0 mmol) under an Ar atmosphere, and the mixture was stirred at 40 °C for 3 h. After cooling to 0 °C, water, 2 M aqueous NaOH solution (8.0 mL), and then 30% H_2O_2 (4.0 mL) were added to the reaction mixture. The mixture was continuously stirred overnight at room temperature. Aqueous Na_2SO_3 solution was added to the reaction mixture at 0 °C, and the mixture was extracted with AcOEt/THF = 6/1. The organic layer was dried with Na_2SO_4, filtered, the filtrate was concentrated under reduced pressure, and the concentrate was purified by SiO_2 column chromatography (CH_2Cl_2 then CH_2Cl_2/MeOH, 50/1, R_f = 0.13) to give 4,12-bis(3-hydroxypropyl)[2.2]PCP **9** as colorless waxy solid. This compound was used for next reaction without further purification. HRMS (FAB-TOF) *m*/*z* calcd. for $C_{22}H_{28}O_2$ 324.2089 [M^+], found 324.2091.

To the diol **9** in CH_2Cl_2 (10.0 mL) was added PPh_3 (1.05 g, 4.00 mmol) and then CBr_4 (1.33 g, 4.01 mmol) at 0 °C, and the mixture was stirred at room temperature for 3 h. The reaction mixture was passed through SiO_2 column chromatography with CH_2Cl_2 and the filtrate was concentrated under reduced pressure. The concentrate was purified by SiO_2 column chromatography (hexane/CH_2Cl_2, 5/1, R_f = 0.38) to give 4,12-bis(3-bromopropyl)[2.2]PCP **10** as colorless powder (0.43 g, 96% from **8**): mp 124−126 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.99 (quint., *J* = 7.2 Hz, 4H), 2.44 (m, 2H), 2.78 (m, 4H), 3.02 (m, 4H), 3.33 (m, 6H), 6.13 (d, *J* = 1.2 Hz, 2H), 6.34 (d, *J* = 7.8 Hz, 2H), 6.62 (dd, *J* = 7.8, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.7, 33.0, 33.4, 33.6, 33.7, 127.1, 133.8, 134.9, 137.4, 139.5, 140.2; HRMS (FAB-TOF) *m*/*z* calcd. for $C_{22}H_{26}Br_2$ 448.0401 [M^+], found 448.0403. Anal. Calcd for $C_{22}H_{26}Br_2$: C, 58.69; H, 5.82. Found: C, 58.73; H, 5.84.

4-(3-Bromopropyl)-12-[3-{*N*-(1,8-naphthalimidyl)}propyl]-[2.2]paracyclophane 11. A mixture of 1,8-naphthalimide (98.9 mg, 0.50 mmol), Cs_2CO_3 (0.33 mg, 1.01 mmol), and DMF (10 mL) was stirred at room temperature for 20 min. To the mixture was added 4,12-bis(3-bromopropyl)[2.2]PCP **10** (225 mg, 0.50 mmol), and the mixture was stirred overnight at room temperature. The reaction mixture was extracted with CH_2Cl_2, and the combined CH_2Cl_2 extract was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The concentrate was purified by SiO_2 column chromatography (hexane/CH_2Cl_2, 1/2, R_f = 0.28) to give 4-(3-bromopropyl)-12-[3-{*N*-(1,8-naphthalimidyl)}-propyl][2.2]PCP **11** as colorless powder (0.14 g, 48%): mp 202−204 °C; IR (Nujol) ν 1660, 1699 (C═O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.91 (quint., *J* = 7.8 Hz, 2H), 1.98 (quint., *J* = 7.2 Hz, 2H), 2.44 (m, 2H), 2.76 (m, 4H), 2.98 (m, 4H), 3.33 (m, 4H), 4.22 (t, *J* = 7.8 Hz, 2H), 6.10 (d, *J* = 1.2 Hz, 1H), 6.16 (d, *J* = 1.2 Hz, 1H), 6.27 (d, *J* = 7.8 Hz, 1H), 6.32 (d, *J* = 7.8 Hz, 1H), 6.53 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 2H), 8.21 (d, *J* = 7.8 Hz, 2H), 8.59 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.6, 32.1, 32.7, 33.0, 33.5, 33.6, 33.7, 33.8, 40.6, 122.8, 126.8, 126.9, 128.2, 131.2, 131.6, 133.7, 133.9, 134.3, 134.9, 137.2, 137.4, 139.2, 139.5, 140.1, 141.0, 164.2; HRMS (FAB-TOF) *m*/*z* calcd. for $C_{34}H_{32}BrNO_2$ 565.1616 [M^+], found 565.1628. Anal. Calcd for $C_{34}H_{32}BrNO_2$: C, 72.08; H, 5.69; N, 2.47. Found: C, 72.26; H, 5.76; N, 2.44.

4-{3-(*N*-Carbazolyl)propyl}-12-[3-{*N*-(1,8-naphthalimidyl)}-propyl][2.2]paracyclophane 1. A mixture of 4-(3-bromopropyl)-12-[3-{*N*-(1,8-naphthalimidyl)}propyl][2.2]PCP **11** (167 mg, 0.29 mmol), carbazole (60.0 mg, 0.36 mmol), *n*-Bu_4NBr (48.2 mg, 0.15 mmol), toluene (6 mL), and a 2 M aqueous NaOH solution (6 mL) was refluxed for 2 d. The reaction mixture was extracted with toluene, the combined toluene extract was dried, filtered, and the filtrate was

dx.doi.org/10.1021/jo5020273 | J. Org. Chem. 2014, 79, 11440−11453

concentrated under reduced pressure. The concentrate was purified by SiO_2 column chromatography (hexane/CH_2Cl_2, 1/3, R_f = 0.35) to give 4-{3-(*N*-carbazolyl)propyl}-12-[3-{*N*-(1,8-naphthalimidyl)}propyl]-[2.2]PCP **1** as yellow powder (186 mg, quant.): mp 100−101 °C; IR (Nujol) ν 1659, 1699 (C═O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.89 (m, 2H), 2.04 (m, 2H), 2.33 (m, 1H), 2.43 (m, 1H), 2.73 (m, 5H), 2.87 (m, 1H), 3.00 (m, 3H), 3.34 (m, 1H), 4.22 (m, 4H), 6.07 (d, J = 1.2 Hz, 1H), 6.10 (d, J = 1.2 Hz, 1H), 6.16 (d, J = 7.2 Hz, 1H), 6.30 (d, J = 7.2 Hz, 1H), 6.31 (dd, J = 7.2, 1.8 Hz, 1H), 6.61 (dd, J = 7.8, 1.8 Hz, 1H), 7.22 (t, J = 7.2 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.44 (m, 2H), 7.74 (dd, J = 8.4, 7.8 Hz, 2H), 8.10 (d, J = 7.2 Hz, 2H), 8.20 (dd, J = 7.8, 1.2 Hz, 2H), 8.59 (dd, J = 7.8, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.6, 29.2, 31.8, 32.0, 32.9, 32.9, 33.4, 33.5, 40.5, 42.5, 108.7, 118.8, 120.3, 122.7, 122.9, 125.6, 126.3, 126.8, 126.9, 128.2, 131.2, 131.6, 133.5, 133.8, 133.9, 134.2, 134.3, 137.1, 137.4, 139.1, 137.4, 140.4, 140.9, 164.1; HRMS (FAB-TOF) m/z calcd. for $C_{46}H_{40}N_2O_2$ 652.3090 [M^+], found 652.3093. Anal. Calcd for $C_{46}H_{40}N_2O_2$: C, 84.63; H, 6.18; N, 4.29. Found: C, 84.62; H, 6.47; N, 4.22.

4-[3-{*N*-(1,8-Naphthalimidyl)}propyl]-12-[3-{*N*-(10*H*-phenothiazinyl)}propyl][2.2]paracyclophane 4. A mixture of 10*H*-phenothiazine (12.4 mg, 0.06 mmol), *t*-BuOK (8.1 mg, 0.07 mmol) and DMF (1.0 mL) was stirred at room temperature for 10 min under an Ar atmosphere. To the mixture was added 4-(3-bromopropyl)-12-[3-{*N*-(1,8-naphthalimidyl)}-propyl][2.2]PCP **11** (28.6 mg, 0.05 mmol), and the mixture was stirred overnight under an Ar atmosphere. The reaction mixture was extracted with CH_2Cl_2, and the combined CH_2Cl_2 extract was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The concentrate was purified by SiO_2 column chromatography (hexane/CH_2Cl_2, 1/2, R_f = 0.45) to give 4-[3-{*N*-(1,8-naphthalimidyl)}propyl]-12-[3-{*N*-(10*H*-phenothiazinyl)}propyl]-[2.2]paracyclophane **4** as yellow powder (9.6 mg, 28%): mp 198−199 °C; IR (Nujol) ν 1654, 1699 (C═O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.91 (m, 4H), 2.39 (m, 2H), 2.56 (m, 1H), 2.72 (m, 3H), 2.90 (m, 4H), 3.04 (m, 1H), 3.32 (m, 1H), 3.82 (br, 2H), 4.20 (t, J = 7.8 Hz, 2H), 6.00 (s, 1H), 6.09 (s, 1H), 6.15 (d, J = 7.8 Hz, 1H), 6.24 (d, J = 7.8 Hz, 1H), 6.40 (d, J = 7.8 Hz, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.79 (d, J = 7.8 Hz, 2H), 6.92 (br, 2H), 7.12 (t, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.74 (t, J = 7.8 Hz, 2H), 8.20 (d, J = 7.8 Hz, 2H), 8.59 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.6, 31.2, 32.0, 32.7, 33.0, 33.5, 40.5, 115.8, 122.5, 122.7, 126.6, 126.7, 126.9, 127.2, 127.5, 128.2, 131.2, 131.6, 133.5, 133.8, 134.2, 134.6, 137.0, 137.5, 139.3, 140.8, 140.9, 164.1; HRMS (FAB-TOF) m/z calcd. for $C_{46}H_{40}N_2O_2S$ 684.2810 [M^+], found 684.2812. Anal. Calcd for $C_{46}H_{40}N_2O_2S$: C, 80.67; H, 5.89; N, 4.09. Found: C, 80.59; H, 6.13; N, 3.92.

4,16-Diallyl[3.3]paracyclophane 13. 4,16-Diallyl[3.3]-paracyclophane **13** was synthesized by the similar procedures as described for **8** (93%). Colorless powder: mp 88−90 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 1.98 (m, 2H), 2.11 (m, 2H), 2.54 (m, 2H), 2.68 (s, 4H), 2.92 (m, 2H), 3.29 (dd, J = 15.6, 6.6 Hz, 2H), 3.51 (dd, J = 15.6, 6.0 Hz, 2H), 5.07 (m, 4H), 5.94 (m, 2H), 6.52 (m, 4H), 6.60 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.2, 32.4, 35.4, 37.6, 115.4, 125.9, 129.8, 131.4, 136.0, 136.3, 137.6, 138.8; HRMS (FAB-TOF) m/z calcd. for $C_{24}H_{28}$ 316.2191 [M^+], found 316.2193. Anal. Calcd for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 90.77; H, 8.90.

4,12-Bis(3-hydroxypropyl)[3.3]PCP 14. This compound was synthesized by the similar procedures to those of **9**, and this compound was used for next reaction without further purification. HRMS (FAB-TOF) m/z calcd. for $C_{24}H_{32}O_2$ 352.2402 [M^+], found 352.2403.

4,16-Bis(3-bromopropyl)[3.3]paracyclophane 15. This compound was synthesized from the diol **9** by the similar procedures to those of **10** (92% from **13**). Colorless powder: mp 147−148 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 2.06 (m, 8H), 2.64 (m, 8H), 2.93 (m, 4H), 3.38 (m, 4H), 6.50 (d, J = 7.8 Hz, 2H), 6.53 (d, J = 7.8 Hz, 2H), 6.58 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.5, 31.4, 32.3, 33.6, 33.8, 35.4, 126.1, 130.0, 131.4, 135.8, 137.2, 138.9; HRMS (FAB-TOF) m/z calcd. for $C_{24}H_{30}Br_2$ 476.0714 [M^+], found 476.0738. Anal. Calcd for $C_{24}H_{30}Br_2$: C, 60.27; H, 6.32. Found: C, 60.17; H, 6.37.

4-(3-Bromopropyl)-16-[3-{*N*-(1,8-naphthalimidyl)}propyl]-[3.3]paracyclophane 16. This compound was synthesized by the similar procedures to those of **11** (43%). Pale yellow powder: mp 143−145 °C; IR (Nujol) ν 1661, 1670 (C═O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.02 (m, 8H), 2.60 (m, 8H), 2.91 (m, 4H), 3.37 (m, 2H), 4.27 (t, J = 7.8 Hz, 2H), 6.40 (d, J = 7.2 Hz, 1H), 6.45 (d, J = 7.8 Hz, 1H), 6.51 (m, 2H), 6.56 (s, 1H), 6.63 (s, 1H), 7.76 (t, J = 7.8 Hz, 2H), 8.21 (d, J = 8.4 Hz, 2H), 8.61 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.5, 28.7, 30.7, 31.5, 32.2, 33.7, 33.8, 35.4, 40.6, 122.8, 125.7, 126.0, 126.9, 128.2, 129.4, 129.9, 131.2, 131.6, 133.8, 135.6, 135.8, 137.0, 137.9, 138.7, 138.9, 164.2; HRMS (FAB-TOF) m/z calcd. for $C_{36}H_{36}BrNO_2$ 593.1929 [M^+], found 593.1929. Anal. Calcd for $C_{36}H_{36}BrNO_2$: C, 72.72; H, 6.10; N, 2.36. Found: C, 72.57; H, 6.13; N, 2.26.

4-{3-(*N*-Carbazolyl)propyl}-16-[3-{*N*-(1,8-naphthalimidyl)}-propyl][3.3]paracyclophane 2. This compound was synthesized by the similar procedures to those of **1** (79%). Yellow powder: mp 80−82 °C; IR (Nujol) ν 1660, 1699 (C═O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.94 (m, 5H), 2.09 (m, 3H), 2.45 (m, 2H), 2.58 (m, 7H), 2.87 (m, 3H), 4.27 (quint. J = 7.8 Hz, 4H), 6.27 (d, J = 8.4 Hz, 1H), 6.38 (d, J = 7.8 Hz, 1H), 6.49 (m, 2H), 6.53 (s, 1H), 6.59 (s, 1H), 7.22 (t, J = 7.8 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.75 (t, J = 7.8 Hz, 2H), 8.10 (d, J = 7.8 Hz, 2H), 8.21 (d, J = 8.4 Hz, 2H), 8.60 (d, J = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.3, 28.7, 29.4, 30.5, 30.7, 32.2, 35.3, 35.4, 40.6, 42.6, 108.7, 118.7, 120.3, 122.7, 122.9, 125.5, 125.6, 125.9, 126.9, 128.2, 129.4, 131.2, 131.6, 133.9, 135.6, 135.8, 137.4, 137.9, 138.6, 138.8, 140.4, 164.2; HRMS (FAB-TOF) m/z calcd. for $C_{48}H_{44}N_2O_2$ 680.3403 [M^+], found 680.3403. Anal. Calcd for $C_{48}H_{44}N_2O_2$: C, 84.67; H, 6.51; N, 4.11. Found: C, 84.33; H, 6.78; N, 3.93.

4-[3-{*N*-(1,8-Naphthalimidyl)}propyl]-16-[3-{*N*-(10*H*-phenothiazinyl)}propyl][3.3]paracyclophane 5. This compound was synthesized by the similar procedures to those of **4** (59%). Yellow powder: mp 229−231 °C; IR (Nujol) ν 1660, 1699 (C═O) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.96 (m, 9H), 2.35 (m, 1H), 2.58 (m, 9H), 2.89 (m, 3H), 3.83 (m, 2H), 4.25 (t, J = 7.8 Hz, 2H), 6.31 (d, J = 7.2 Hz, 1H), 6.37 (d, J = 7.8 Hz, 1H), 6.46 (m, 3H), 6.58 (s, 1H), 6.80 (d, J = 7.8 Hz, 2H), 6.91 (t, J = 7.8 Hz, 2H), 7.11 (t, J = 7.2 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 7.75 (t, J = 7.8 Hz, 2H), 8.21 (d, J = 8.4 Hz, 2H), 8.60 (d, J = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.5, 28.6, 28.7, 30.0, 30.7, 35.3, 40.6, 46.5, 115.8, 122.4, 133.8, 125.6, 125.7, 126.9, 127.1, 127.4, 128.2, 129.3, 130.1, 131.2, 131.6, 133.8, 135.6, 135.8, 137.8, 137.9, 138.6, 138.7, 145.3, 164.2; HRMS (FAB-TOF) m/z calcd. for $C_{48}H_{44}N_2O_2S$ 712.3123 [M^+], found 712.3109. Anal. Calcd for $C_{48}H_{44}N_2O_2S$: C, 80.86; H, 6.22; N, 3.93. Found: C, 80.74; H, 6.32; N, 3.79.

4,12-Divinyl[2.2]paracyclophane 17. This compound was synthesized according to the reported procedures.[26] A mixture of 4,12-dibromo[2.2]PCP **7** (1.10 g, 3.00 mmol), vinyltributyltin (5.76 g, 18.2 mmol), $Pd(PPh_3)_4$ (0.52 g, 0.45 mmol), and toluene (120 mL) was stirred at 100 °C for 1 d under an Ar atmosphere. The reaction mixture was passed through a silica gel containing 10 wt % K_2CO_3 with toluene to remove tin halides, and the eluate was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography (hexane/CH_2Cl_2, 5/1, R_f = 0.33) to give 4,12-divinyl[2.2]PCP **17** as colorless powder (0.43 g, 56%): ^1H NMR (600 MHz, $CDCl_3$) δ 2.83 (m, 2H), 2.96 (m, 2H), 3.05 (m, 2H), 3.47 (m, 2H), 5.28 (d, J = 10.8 Hz, 2H), 5.52 (d, J = 17.4 Hz), 6.33 (d, J = 7.2 Hz, 2H), 6.55 (s, 2H), 6.65 (d, J = 7 0.8 Hz, 2H), 6.82 (dd, J = 17.4, 10.8 Hz, 2H) (lit.[27] δ 2.81, 2.94, 3.03, 3.45, 5.27, 5.51, 6.31, 6.54, 6.65, 6.80.); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.0, 34.2, 114.3, 129.3, 130.1, 133.4, 135.3, 137.7, 139.4; HRMS(FAB-TOF) m/z calcd. for $C_{20}H_{20}$ 260.1565 [M^+], found 260.1562.

4,12-Bis(2-bromoethyl)[2.2]paracyclophane 19. 4,12-Divinyl-[2.2]PCP **17** (0.26 g, 1.00 mmol) was dissolved in a 0.5 M THF solution of 9-BBN (6.0 mL, 3.0 mmol) under an Ar atmosphere. The mixture was stirred at 60 °C overnight. After cooling to 0 °C, water, a 2 M aqueous NaOH solution (8.0 mL), and aqueous H_2O_2 (4.0 mL) were successively added to the reaction mixture, and the mixture was continuously stirred at room temperature for 6 h. Aqueous Na_2SO_3 solution was added to the reaction mixture at 0 °C and the mixture was extracted with AcOEt/THF = 6/1. The combined AcOEt/THF extract was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to give crude 4,12-bis(2-hydroxyethyl)[2.2]PCP **18**, which was used for the next reaction without further purification. HRMS

dx.doi.org/10.1021/jo5020273 | J. Org. Chem. 2014, 79, 11440−11453

(FAB-TOF) m/z calcd. for $C_{20}H_{25}O_2$ 297.1855 [M + H$^+$], found 297.1859.

To the diol **18** in CH_2Cl_2 (10 mL) were added PPh_3 (1.05 g, 4.00 mmol) and CBr_4 (1.34 g, 4.04 mmol) at 0 °C, and the mixture was stirred at room temperature for 1.5 h. Since the TLC (SiO_2) analysis of the reaction mixture indicated the presence of the starting compounds, additional amounts of PPh_3 (1.05 g, 4.00 mmol) and CBr_4 (1.34 g, 4.04 mmol) were added and the mixture was stirred at the same temperature for an additional 1.5 h. Then the reaction mixture was passed through a SiO_2 column with CH_2Cl_2, and the eluate was concentrated under reduced pressure. The concentrate was purified by SiO_2 column chromatography (hexane/CH_2Cl_2, 5/1, R_f = 0.30) to give 4,12-bis(2-bromoethyl)[2.2]PCP **19** as colorless powder (0.38 g, 85% from **17**): mp 201−202 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.83 (m, 4H), 3.05 (m, 4H), 3.16 (m, 2H), 3.33 (m, 4H), 3.39 (m, 2H), 6.16 (d, J = 1.8 Hz, 2H), 6.38 (d, J = 7.8 Hz, 2H), 6.64 (dd, J = 7.8, 1.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.1, 32.7, 33.5, 38.5, 127.9, 134.0, 135.2, 137.4, 138.6, 139.6; HRMS (FAB-TOF) m/z calcd. for $C_{20}H_{22}Br_2$ 420.0088 [M$^+$], found 420.0094. Anal. Calcd for $C_{20}H_{22}Br_2$: C, 56.90; H, 5.25. Found: C, 57.13; H, 5.12.

4-(2-Bromoethyl)-12-[2-{*N*-(1,8-naphthalimidyl)}ethyl][2.2]-paracyclophane 20. A mixture of 1,8-naphthalimide (39.3 mg, 0.20 mmol), Cs_2CO_3 (130 mg, 0.40 mmol), and DMF (4 mL) was stirred at room temperature for 10 min. To the mixture was added the dibromide **19** (84.5 mg, 0.20 mmol), and the mixture was stirred overnight. The reaction mixture was extracted with CH_2Cl_2, and the combined CH_2Cl_2 extract was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The concentrate was purified by SiO_2 column chromatography (hexane/CH_2Cl_2, 1/2, R_f = 0.31) to give 4-(2-bromoethyl)-12-[2-{*N*-(1,8-naphthalimidyl)}ethyl][2.2]PCP **20** as colorless powder (49.2 mg, 46%): mp 242−244 °C; IR (Nujol) ν 1655, 1670 (C=O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.71 (m, 1H), 2.86 (m, 3H), 3.08 (m, 6H), 3.32 (m, 2H), 3.38 (m, 1H), 3.71 (m, 1H), 4.20 (m, 2H), 6.15 (s, 1H), 6.34 (s, 1H), 6.36 (d, J = 7.8 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 6.62 (m, 2H), 7.79 (t, J = 7.8 Hz, 1H), 8.25 (d, J = 7.8 Hz, 1H), 8.65 (d, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.1, 32.9, 33.3, 33.7, 38.7, 41.1, 122.8, 127.0, 127.6, 128.0, 128.3, 131.3, 131.7, 133.9, 134.0, 134.2, 135.1, 135.6, 137.4, 138.1, 138.4, 138.6, 139.4, 140.0, 164.2; HRMS (FAB-TOF) m/z calcd. for $C_{32}H_{28}BrNO_2$ 537.1303 [M$^+$], found 537.1333. Anal. Calcd for $C_{32}H_{28}BrNO_2$: C, 71.38; H, 5.24; N, 2.60. Found: C, 71.21; H, 5.26; N, 2.63.

4-{2-(*N*-Carbazolyl)ethyl}-12-[2-{*N*-(1,8-naphthalimidyl)}-ethyl][2.2]paracyclophane 3. A mixture of the bromide **20** (51.6 mg, 0.10 mmol), carbazole (20.1 mg, 0.12 mmol), n-Bu_4NBr (16.6 mg, 0.051 mmol), toluene (2 mL), and a 2 M aqueous NaOH solution. (2 mL) was refluxed for 2 d. The reaction mixture was extracted with toluene, the combined toluene extract was dried, filtered, and the filtrate was concentrated under reduced pressure. The concentrate was purified by SiO_2 column chromatography (hexane/CH_2Cl_2, 1/3, R_f = 0.53), followed by recycling preparative HPLC (GPC, JAIGEL 1H+2H, $CHCl_3$) to give 4-{2-(*N*-carbazolyl)ethyl}-12-[2-{*N*-(1,8-naphthalimidyl)}ethyl][2.2]PCP **3** as yellow powder (29.0 mg, 48%): mp 233−234 °C; IR (Nujol) ν 1654, 1670 (C=O) cm^{-1}; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 2.69 (m, 1H), 2.80 (m, 3H), 3.03 (m, 7H), 3.36 (t, J = 7.2 Hz, 1H), 3.66 (t, J = 7.2 Hz, 1H), 4.15 (m, 2H), 4.33 (m, 2H), 6.23 (s, 1H), 6.29 (s, 1H), 6.36 (m, 2H), 6.52 (d, J = 7.2 Hz, 1H), 6.62 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 7.8 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.80 (t, J = 7.8 Hz, 2H), 8.10 (d, J = 7.8 Hz, 2H), 8.27 (d, J = 7.8 Hz, 2H), 8.61 (d, J = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 31.0, 33.2, 33.4, 33.6, 34.0, 34.4, 41.3, 44.3, 109.0, 119.2, 120.7, 123.2, 123.3, 126.1, 127.4, 127.9, 128.1, 131.4, 132.2, 134.3, 134.4, 134.5, 135.8, 138.0, 138.5, 138.7, 138.9, 139.9, 140.4, 140.6, 164.4; HRMS (FAB-TOF) m/z calcd. for $C_{44}H_{36}N_2O_2$ 624.2777 [M$^+$], found 624.2780. Anal. Calcd for $C_{44}H_{36}N_2O_2$: C, 84.59; H, 5.81; N, 4.48. Found: C, 84.41; H, 5.77; N, 4.46.

4-[(*E*)-2-{4-(2,1,3-Benzothiadiazolyl)}vinyl]-12-vinyl[2.2]-paracyclophane 21. A mixture of 4,12-divinyl[2.2]PCP **17** (0.26 g, 1.01 mmol), 4-bromo-2,1,3-benzothiadiazole (0.22 g, 1.02 mmol), $Pd(OAc)_2$ (23.5 mg, 0.10 mmol), K_2CO_3 (0.69 g, 4.97 mmol), n-Bu_4NBr (0.32 g, 1.00 mmol), and DMF (30 mL) was stirred at 100 °C for 2 d under an Ar atmosphere. The reaction mixture was filtered through a Celite pad, and the filtrate was extracted with AcOEt. The combined AcOEt extract was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography (hexane/CH_2Cl_2, 2/1, R_f = 0.13). The eluate was concentrated under reduced pressure, and the concentrate was washed with MeOH to give 4-[(*E*)-2-{4-(2,1,3-benzothiadiazolyl)}vinyl]-12-vinyl[2.2]PCP **21** as yellow powder (0.16 g, 39%). Yellow powder (toluene and MeOH): mp 185−188 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.96 (m, 3H), 3.11 (m, 3H), 3.51 (m, 1H), 3.72 (m, 1H), 5.31 (dd, J = 10.8, 1.2 Hz, 1H), 5.55 (dd, J = 17.4, 1.2 Hz, 1H), 6.42 (d, J = 7.8 Hz, 2H), 6.60 (d, J = 1.8 Hz, 1H), 6.72 (td, J = 7.8, 1.8 Hz, 2H), 6.84 (m, 2H), 7.36 (d, J = 16.2 Hz, 1H), 7.64 (dd, J = 8.4, 7.2 Hz, 1H), 7.69 (d, J = 6.6 Hz), 7.92 (dd, J = 8.4, 0.6 Hz, 1H), 8.23 (d, J = 16.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.0, 33.5, 34.3, 34.4, 114.4, 119.9, 124.9, 126.6, 129.7, 129.8, 130.2, 130.3, 131.4, 132.7, 133.4, 133.7, 135.3, 137.5, 137.8, 139.0, 139.4, 139.7, 153.4, 155.8; HRMS (FAB-TOF) m/z calcd. for $C_{26}H_{22}N_2S$ 394.1504 [M$^+$], found 394.1494. Anal. Calcd for $C_{26}H_{22}N_2S$: C, 79.15; H, 5.62; N, 7.10. Found: C, 78.94; H, 5.69; N, 6.99.

4-[(*E*)-2-{4-(2,1,3-Benzothiadiazolyl)}vinyl]-12-[(*E*)-2-{3-(10-methyl-10*H*-phenothiazinyl)}vinyl][2.2]paracyclophane 22. A mixture of 4-[(*E*)-2-{4-(2,1,3-benzothiadiazolyl)}vinyl]-12-vinyl[2.2]-PCP **21** (39.4 mg, 0.10 mmol), 3-bromo-10-methyl-10*H*-phenothiazine (35.4 mg, 0.12 mmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (4.1 mg, 0.005 mmol), K_2CO_3 (69.4 mg, 0.50 mmol), n-Bu_4NBr (32.1 mg, 0.10 mmol), and DMF (10 mL) was stirred at 100 °C for 1d under an Ar atmosphere. The reaction mixture was filtered through a Celite pad, and the filtrate was extracted with AcOEt. The combined AcOEt extract was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography (hexane/CH_2Cl_2, 3/2, R_f = 0.39). The eluate was concentrated under reduced pressure, and the concentrate was washed with MeOH to give 4-[(*E*)-2-{4-(2,1,3-benzothiadiazolyl)}vinyl]-12-[(*E*)-2-{3-(10-methyl-10*H*-phenothiazinlyl)}vinyl][2.2]PCP **22** as yellow powder (35.9 mg, 59%). Yellow powder (toluene and MeOH): mp 238−239 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.98 (m, 3H), 3.14 (m, 3H), 3.42 (s, 3H), 3.61 (m, 1H), 3.73 (m, 1H), 6.44 (d, J = 1.2 Hz, 1H), 6.45 (d, J = 1.2 Hz, 1H), 6.67 (d, J = 1.2 Hz, 1H), 6.69 (m, 2H), 6.78 (d, J = 16.2 Hz, 1H), 6.82 (d, J = 1.2 Hz, 1H), 6.84 (m, 2H), 6.96 (td, J = 7.2, 1.2 Hz, 1H), 7.09 (d, J = 16.2 Hz, 1H), 7.20 (m, 2H), 7.36 (m, 2H), 7.41 (d, J = 1.8 Hz, 1H), 7.64 (dd, J = 8.4, 6.6 Hz, 1H), 7.69 (d, J = 6.6 Hz, 1H), 7.93 (dd, J = 8.4, 0.6 Hz, 1H), 8.25 (d, J = 16.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.4, 33.5, 34.5, 35.4, 114.1, 119.9, 122.6, 123.0, 123.8, 124.5, 124.9, 125.5, 126.2, 126.7, 127.2, 127.5, 128.1, 129.5, 129.7, 130.0, 130.4, 131.4, 132.6, 132.7, 133.6, 137.5, 138.0, 139.0, 139.5, 139.6, 145.2, 145.5, 153.4, 155.8; HRMS (FAB-TOF) m/z calcd. for $C_{39}H_{31}N_3S_2$ 605.1959 [M$^+$], found 605.1957. Anal. Calcd for $C_{39}H_{31}N_3S_2$: C, 77.32; H, 5.16; N, 6.94. Found: C, 77.12; H, 5.07; N, 6.88.

4-[2-{4-(2,1,3-Benzothiadiazolyl)}ethyl]-12-[2-{3-(10-methyl-10*H*-phenothiazinlyl)}ethyl][2.2]paracyclophane 6. A mixture of 4-[(*E*)-2-{4-(2,1,3-benzothiadiazolyl)}vinyl]-12-[(*E*)-2-{3-(10-methyl-10*H*-phenothiazinlyl)}vinyl][2.2]PCP **22** (61.3 mg, 0.10 mmol), 80% hydrazine monohydrate (0.62 mL, 10.0 mmol), and diethylene glycol (65 mL) was stirred at 100 °C for 20 h. After cooling to room temperature, the reaction mixture was extracted with AcOEt. The combined AcOEt extract was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2, 1/1, R_f = 0.39) and GPC with $CHCl_3$ to give 4-[2-{4-(2,1,3-benzothiadiazolyl)}ethyl]-12-[2-{3-(10-methyl-10*H*-phenothiazinlyl)}ethyl][2.2]PCP **6** as yellow powder (25.2 mg, 41%). Yellow powder (toluene and MeOH): mp 116−118 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.52 (m, 1H), 2.61 (m, 2H), 2.80 (m, 4H), 3.00 (m, 4H), 3.11 (m, 1H), 3.25 (m, 3H), 3.37 (s, 3H), 3.43 (m, 1H), 6.14 (s, 1H), 6.19 (s, 1H), 6.59 (m, 2H), 6.74 (d, J = 7.8 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.94 (m, 2H), 7.01 (d, J = 1.2 Hz, 1H), 7.17 (m, 2H), 7.25 (1H), 7.49 (dd, J = 9.0, 8.4 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.0, 33.6, 35.2, 35.3, 36.0, 37.1, 114.0, 119.3, 122.3, 123.3, 123.4, 127.0, 127.2, 127.3, 127.4, 129.6,

dx.doi.org/10.1021/jo5020273 | J. Org. Chem. 2014, 79, 11440−11453

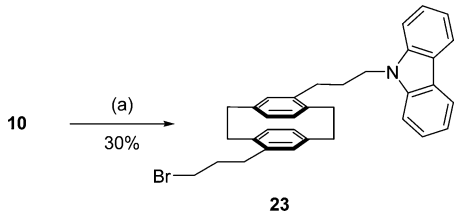
133.8, 134.5, 134.6, 135.6, 136.6, 137.2, 137.4, 139.4, 139.5, 141.2, 141.3, 143.9, 146.0, 154.9, 155.3; HRMS (FAB-TOF) m/z calcd. for $C_{39}H_{35}N_3S_2$ 609.2272 [M^+], found 609.2270. Anal. Calcd for $C_{39}H_{35}N_3S_2$: C, 76.81; H, 5.79; N, 6.89. Found: C, 76.85; H, 5.71; N, 6.77.

Experimental procedures of the reference compounds **23**−**25** are also described.

Synthesis of the Reference Compounds 23−**25.** *4,12-Dibromo[2.2]paracyclophane **7**.* This compound was synthesized according to the reported procedures.[18] To a mixture of [2.2]PCP (5.04 g, 24.2 mmol) and CH_2Cl_2 (80 mL) was added a CH_2Cl_2 (20 mL) solution of Br_2 (3.0 mL, 59 mmol) over a period of ca. 30 min at reflux, and the mixture was stirred overnight at reflux. The reaction mixture was quenched by aq. Na_2SO_3, and the solution was extracted with CH_2Cl_2. The combined CH_2Cl_2 extract was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The concentrate was purified by recrystallization from $CHCl_3$ to give 4,12-dibromo[2.2]PCP **7** as colorless solid (2.19 g, 25%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.85 (m, 2H), 2.94 (m, 2H), 3.16 (m, 2H), 3.50 (m, 2H), 6.44 (d, J = 7.8 Hz, 2H), 6.51 (d, J = 1.2 Hz, 2H), 7.14 (dd, J = 7.8, 1.2 Hz, 2H) (lit.[18] δ 2.97, 3.19, 3.49, 6.43, 6.51, 7.13.); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.8, 35.4, 126.7, 128.3, 134.1, 137.3, 138.5, 141.2.

*4-(3-Bromopropyl)-12-{3-(N-carbazolyl)propyl}[2.2]paracyclophane **23**.* A mixture of 4,12-bis(3-bromopropyl)[2.2]PCP **10** (225 mg, 0.50 mmol), carbazole (83.5 mg, 0.50 mmol), n-Bu_4NBr (82.3 mg, 0.26 mmol), toluene (10 mL), and a 2 M aqueous NaOH solution (10 mL) was refluxed for 2 d. The reaction mixture was extracted with CH_2Cl_2, the combined CH_2Cl_2 extract was dried, filtered, and the filtrate was concentrated under reduced pressure. The concentrate was purified by SiO_2 column chromatography (hexane/CH_2Cl_2, 1/3, R_f = 0.41) to give 4-(3-bromopropyl)-12-{3-(*N*-carbazolyl)propyl}[2.2]PCP **23** as colorless powder (101 mg, 38%; Scheme 4): mp 181−182 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.97 (quint., J = 7.2 Hz, 2H), 2.05 (quint., J = 7.2 Hz, 2H), 2.33 (quint., J = 7.2 Hz, 1H), 2.42 (quint., J = 7.2 Hz, 1H), 2.68 (m, 5H), 3.00 (m, 1H), 3.05 (m, 3H), 3.31 (m, 3H), 4.26 (m, 2H), 6.06 (s, 1H), 6.08 (s, 1H), 6.22 (d, J = 7.8 Hz, 1H), 6.31 (d, J = 7.8 Hz, 1H), 6.36 (d, J = 7.8 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 7.22 (t, J = 7.2 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 2 Hz, 2H), 8.11 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.2, 31.8, 32.7, 32.9, 33.3, 33.4, 33.6, 33.7, 42.5, 108.7, 118.8, 120.3, 122.9, 125.6, 126.7, 127.0, 133.7, 133.8, 134.3, 134.8, 137.3, 137.4, 139.3, 139.4, 140.1, 140.4, 140.5; HRMS (FAB-TOF) m/z calcd. For $C_{34}H_{34}BrN$ 535.1875 [M^+], found 535.1879. Anal. Calcd for $C_{34}H_{34}BrN$: C, 76.11; H, 6.39; N, 2.61. Found: C, 75.96; H, 6.41; N, 2.51.

Scheme 4. Synthesis of the Reference Compounds, Cz-$(CH_2)_3$-[2.2]PCP-$(CH_2)_3$Br 23[a]



[a]Reagents and conditions: (a) carbazole, n-Bu_4NBr, toluene, 2 M NaOH aq., reflux, 2 d.

Synthesis of [2.2]PCP-$(CH_2)_2$-BTD 24, and Me-PTZ-$(CH_2)_2$-[2.2]PCP 25 (Scheme 5). *{4-(2,1,3-Benzothiadiazolyl)}methyltriphenylphosphonium bromide **27**.* To a mixture of 2-methyl-6-nitroaniline (4.57 g, 30.0 mmol) and EtOH (100 mL) was added Pd−C-ethylene diamine adduct (0.21 g), and the mixture was stirred at room temperature overnight under hydrogen atmosphere (1 atm). The reaction mixture was filtered through a Celite pad, and the filtrate was concentrated under reduced pressure to give 2,3-diaminotoluene as yellow solid. This compound was used for the next reaction without further purification.

To a toluene solution (40 mL) of 2,3-diaminotoluene was added dropwise $SOCl_2$ (11.0 mL, 152 mmol) over a period of ca. 3 min with vigorous stirring, and the mixture was refluxed overnight. After cooling to room temperature, water was added to the reaction mixture to quench excess $SOCl_2$. The toluene was removed, and the residue was purified by steam-distillation, followed by silica gel column chromatography (hexane, R_f = 0.13) to give 4-methyl-2,1,3-benzothiadiazole as pale yellow liquid (3.38 g, 75% from 2-methyl-6-nitroaniline): ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.75 (s, 3H), 7.35 (d, J = 6.6 Hz, 1H), 7.49 (dd, J = 9.0, 6.6 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H) (lit.[28] δ 2.65, 7.10, 7.30, 7.36.); ^{13}C NMR (150 MHz, $CDCl_3$) δ 17.9, 119.0, 127.9, 129.5, 131.7, 155.0, 155.4 (lit.[28] δ 17.6, 118.8, 127.7, 129.3, 131.5, 154.9, 155.4.); HRMS (EI-TOF) m/z calcd. for $C_7H_6N_2S$ 150.0252 [M^+], found 150.0289.

A mixture of 4-methyl-2,1,3-benzothiadiazole (1.54 g, 10.3 mmol), NBS (2.20 g, 12.4 mmol), AIBN (85.0 mg, 0.52 mmol), and CH_2Cl_2 (50 mL) was refluxed overnight. The reaction mixture was extracted with CH_2Cl_2, and the organic layer was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The concentrate was purified by recrystallization from $CHCl_3$ to give 4-bromomethyl-2,1,3-benzothiadiazole **26** as colorless solid (1.57 g, 67%): mp 91−92 °C (lit.[29] 90.5−91.5 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.00 (s, 2H), 7.57 (dd, J = 8.4, 6.6 Hz, 1H), 7.65 (d, J = 6.6 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.3, 121.9, 129.3, 130.8, 153.4, 155.1; HRMS (FAB-TOF) m/z calcd. for $C_7H_6BrN_2S$ 228.9435 [M + H^+], found 228.9428.

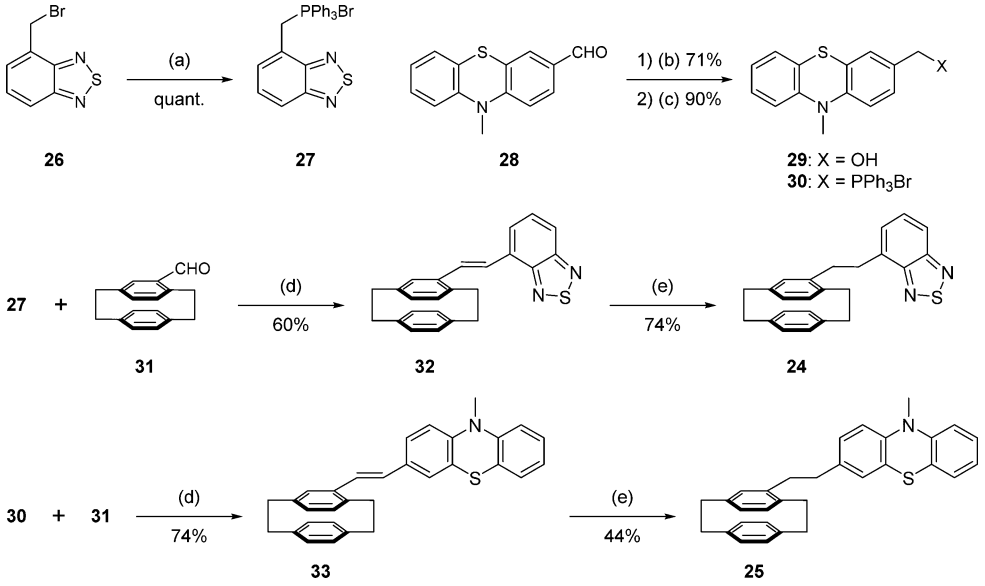
A mixture of 4-bromomethyl-2,1,3-benzothiadiazole **26** (0.69 g, 3.01 mmol), PPh_3 (0.87 g, 3.31 mmol), and toluene (10 mL) was stirred at 100 °C overnight. The precipitate was collected by filtration, and washed with toluene to give the triphenylphosphonium bromide **27** as colorless powder (1.48 g, quant.): mp 229−230 °C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 5.92 (d, J = 15.0 Hz, 2H), 7.51 (t, J = 8.4 Hz, 1H), 7.58 (td, J = 7.8, 3.6 Hz, 6H), 7.77 (m, 10H), 7.91 (dd, J = 9.0, 3.0 Hz, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 27.1 (d, J = 48.0 Hz), 117.3, 117.9, 121.0 (d, J = 9.0 Hz), 121.8 (d, J = 3.0 Hz), 129.6 (d, J = 4.5 Hz), 130.0 (d, J = 13.5 Hz), 132.4 (d, J = 7.5 Hz), 134.3 (d, J = 10.5 Hz), 135.1 (d, J = 3.0 Hz), 154.6 (d, J = 58.5 Hz); HRMS (FAB-TOF) m/z calcd. for $C_{25}H_{20}N_2PS$ 411.1085 [M − Br^+], found 411.1078.

*{3-(10-Methyl-10H-phenothiazinyl)}methyltriphenylphosphonium bromide **30**.* To a mixture of 10-methyl-10*H*-phenothiazine (4.28 g, 20.1 mmol), DMF (7.8 mL, 100 mmol), and $CHCl_3$ (50 mL) was added dropwise $POCl_3$ (10.0 mL, 107 mmol) over a period of ca. 3 min with vigorous stirring at 0 °C. The mixture was then refluxed overnight. Water was added slowly to the cooled reaction mixture at 0 °C to quench excess $POCl_3$, and the mixture was extracted with $CHCl_3$. The combined $CHCl_3$ extract was dried with Na_2SO_4, filtered, the filtrate was concentrated under reduced pressure, and the concentrate was purified by silica gel column chromatography (hexane/CH_2Cl_2, 2/1 then 1/1, R_f = 0.03, 0.12) to give 10-methyl-10*H*-phenothazine-3-carboxyaldehyde **28** as greenish yellow solid (4.16 g, 86%): mp 81−83 °C (lit.[30] 86−87 °C); IR (Nujol) ν 1684 (C═O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.44 (s, 3H), 6.86 (m, 2H), 6.99 (td, J = 7.2, 1.2 Hz, 1H), 7.14 (dd, J = 7.2, 1.2 Hz, 1H), 7.20 (m, 1H), 7.61 (d, J = 1.8 Hz, 1H), 7.67 (dd, J = 8.4, 1.8 Hz, 1H), 9.81 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.8, 113.7, 114.8, 122.6, 123.6, 124.0, 127.3, 127.8, 128.0, 130.4, 131.2, 144.1, 151.1, 190.1; HRMS (FAB-TOF) m/z calcd. for $C_{14}H_{11}NOS$ 241.0561 [M^+], found 241.0570.

To 10-methyl-10*H*-phenothazine-3-carboxyaldehyde **28** (2.52 g, 10.4 mmol) in MeOH (200 mL) was added $NaBH_4$ (1.19 g, 31.5 mmol), and the mixture was stirred at room temperature for 1.5 h. The reaction was quenched by the addition of water, and extracted with AcOEt. The organic layer was dried with Na_2SO_4, filtered, the filtrate was concentrated under reduced pressure, and the concentrate was purified by silica gel column chromatography (CH_2Cl_2, R_f = 0.13) to give 3-hydroxymethyl-10-methyl-10*H*-phenothiazine **29** as colorless solid (1.80 g, 71%): mp 138−139 °C (lit.[30] 133−133.5 °C); ^{1}H NMR (600 MHz, Acetone-d_6) δ 3.38 (s, 3H), 4.53 (d, J = 6.0 Hz, 2H), 6.93 (m, 3H), 7.14 (m, 2H), 7.19 (m, 2H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 35.7, 64.0, 114.9, 115.1, 123.2, 123.7, 123.9, 126.1, 126.9, 127.6, 128.5, 137.8, 145.6, 146.9; HRMS (FAB-TOF) m/z calcd. for $C_{14}H_{13}NOS$ 243.0718 [M^+], found 243.0716.

dx.doi.org/10.1021/jo5020273 | J. Org. Chem. 2014, 79, 11440−11453

Scheme 5. Syntheses of [2.2]PCP-$(CH_2)_2$-BTD 24, Me-PTZ-$(CH_2)_2$-[2.2]PCP 25[a]



[a]Reagents and conditions: (a) PPh_3, toluene, reflux, overnight; (b) $NaBH_4$, MeOH, rt; (c) PPh_3·HBr, $CHCl_3$, reflux; (d) NaHMDS/THF, 0 °C, 30 min then THF, rt; (e) NH_2NH_2·H_2O, diethylene glycol, 100 °C, 1 d.

A mixture of 3-hydroxymethyl-10-methyl-10*H*-phenothiazine **29** (1.80 g, 7.40 mmol), triphenylphosphine hydrobromide (2.54 g, 7.40 mmol), and $CHCl_3$ (100 mL) was refluxed overnight. The solvent was removed under reduced pressure. To the residue was added toluene, and the precipitate was collected by filtration, and washed with toluene to give the triphenylphosphonium bromide **30** as pale yellow powder (3.80 g, 90%): mp >243 °C (decomp.); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 3.24 (s, 3H), 5.21 (d, J = 13.8 Hz, 2H), 6.54 (dd, J = 8.4, 2.4 Hz, 1H), 6.65 (s, 1H), 6.80 (d, J = 7.8 Hz, 1H), 6.90 (t, J = 7.2 Hz, 1H), 6.96 (m, 1H), 7.01 (d, J = 7.2 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.63 (m, 6H), 7.73 (m, 6H), 7.79 (m, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 29.9 (d, J = 46.5 Hz), 35.20, 114.1 (d, J = 3.0 Hz), 114.3, 117.4, 118.0, 120.6 (d, J = 7.5 Hz), 122.6 (d, J = 19.5 Hz), 123.6, 126.9, 127.6, 129.3, 130.0 (d, J = 13.5 Hz), 130.7 (d, J = 6.0 Hz), 134.4 (d, J = 10.5 Hz), 135.0 (d, J = 3.0 Hz), 154.2, 145.9; HRMS (FAB-TOF) m/z calcd. for $C_{32}H_{27}NPS$ 488.1602 [M − Br$^+$], found 488.1602.

4-Formyl[2.2]paracyclophane ***31***. To [2.2]PCP (1.05 g, 5.04 mmol) in CH_2Cl_2 (65 mL) were added successively a 1 M CH_2Cl_2 solution of $TiCl_4$ (10.0 mL, 10.0 mmol) and CH_3OCHCl_2 (0.66 mL, 7.46 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 d. The reaction mixture was poured into ice−water, and the mixture was stirred for 2 h. The reaction mixture was extracted with CH_2Cl_2, and combined CH_2Cl_2 extract was dried with Na_2SO_4, filtered, the filtrate was concentrated under reduced pressure, and the concentrate was purified by silica gel column chromatography (hexane/CH_2Cl_2, 2/1, R_f = 0.03) to give 4-formly[2.2]PCP **31** as colorless powder (0.87 g, 73%): mp 144−145 °C (lit.[31] 142−145 °C); IR (Nujol) ν 1681 (C═O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.96 (m, 1H), 3.07 (m, 3H), 3.21 (m, 2H), 3.27 (m, 1H), 4.10 (m, 1H), 6.38 (dd, J = 7.8, 1.8 Hz, 1H), 6.43 (dd, J = 7.8, 1.8 Hz, 1H), 6.50 (dd, J = 7.8, 1.8 Hz, 1H), 6.56 (dd, J = 7.8, 1.8 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 6.73 (dd, J = 7.8, 1.8 Hz, 1H), 7.01 (d, J = 1.8 Hz, 1H), 9.95 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.6, 35.0, 35.2, 35.3, 132.2, 132.4, 132.9, 133.3, 136.1, 136.3, 136.6, 138.1, 139.5, 140.7, 143.2, 191.9; HRMS (FAB-TOF) m/z calcd. for $C_{17}H_{16}O$ 236.1201 [M$^+$], found 236.1182.

4-[(E)-2-{4-(2,1,3-Benzothiadiazolyl)}vinyl][2.2]paracyclophane ***32***. To {4-(2,1,3-benzothiadiazolyl)}methyltriphenylphosphonium bromide **27** (0.37 g, 0.75 mmol) in THF (5.0 mL) was added 1.1 M THF solution of sodium hexamethyldisilazide (NaHMDS) (0.70 mL, 0.77 mmol) at 0 °C under an Ar atmosphere, and the mixture was continuously stirred at the same temperature for 30 min. 4-Formly[2.2]PCP **31** (0.12 g, 0.50 mmol) in THF (5.0 mL) was added to the mixture, and the mixture was stirred at room temperature for 3 h. The reaction mixture was extracted with AcOEt, and the combined AcOEt extract was dried with Na_2SO_4, filtered, the filtrate was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography (hexane/CH_2Cl_2, 3/1, R_f = 0.09) to give 4-[(*E*)-2-{4-(2,1,3-benzothiadiazolyl)}vinyl][2.2]PCP **32** as yellow powder (0.11 g, 60%): mp 170−171 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.93 (m, 1H), 3.13 (m, 6H), 3.72 (m, 1H), 6.52 (m, 5H), 6.75 (dd, J = 7.8, 1.8 Hz, 1H), 6.80 (d, J = 1.2 Hz, 1H), 7.36 (d, J = 16.2 Hz, 1H), 7.64 (dd, J = 8.4, 7.2 Hz, 1H), 7.68 (d, J = 7.2 Hz, 1H), 7.91 (dd, J = 8.4, 0.6 Hz, 1H), 8.21 (d, J = 15.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.2, 34.9, 35.3, 35.5, 119.9, 124.8, 126.7, 129.7, 130.1, 130.3, 131.4, 131.8, 132.4, 132.5, 133.1, 135.0, 137.6, 139.3, 139.4, 140.1, 153.4, 155.8; HRMS (FAB-TOF) m/z calcd. for $C_{24}H_{20}N_2S$ 368.1347 [M$^+$], found 368.1354. Anal. Calcd for $C_{24}H_{20}N_2S$: C, 78.23; H, 5.47; N, 7.60. Found: C, 78.15; H, 5.46; N, 7.53.

4-[2-{4-(2,1,3-Benzothiadiazolyl)}ethyl][2.2]paracyclophane ***24***. A mixture of 4-[(*E*)-2-{4-(2,1,3-benzothiadiazolyl)}vinyl][2.2]PCP **32** (36.9 mg, 0.10 mmol), hydrazine monohydrate (0.31 mL, 5.0 mmol), and diethylene glycol (10 mL) was stirred at 100 °C overnight. The reaction was checked by NMR, 80% hydrazine monohydrate (0.31 mL, 5.0 mmol) was additionally added to the reaction mixture because the starting material was remained, and the mixture was continuously stirred at the same temperature for 1 d. After cooling to room temperature, the reaction mixture was extracted with AcOEt. The combined AcOEt extract was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2, 2/1, R_f = 0.22) and GPC with $CHCl_3$ to give 4-[2-{4-(2,1,3-benzothiadiazolyl)}ethyl][2.2]PCP **24** as colorless solid (27.5 mg, 74%). Colorless solids (toluene and MeOH): mp 105−106 °C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 2.78 (m, 2H), 3.03 (m, 8H), 3.20 (m, 1H), 3.26 (m, 1H), 3.46 (m, 1H), 6.22 (s, 1H), 6.39 (d, J = 7.8 Hz, 1H), 6.43 (m, 2H), 6.46 (d, J = 7.8 Hz, 1H), 6.66 (d, J = 7.8 Hz), 7.30 (d, J = 6.6 Hz, 1H), 7.51 (m, 1H), 7.85 (d, J = 9.0 Hz); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 33.5, 33.6, 34.2, 34.9, 35.0, 35.3, 119.2, 127.4, 128.9, 129.6, 130.6, 132.2, 133.2, 133.4, 134.5, 134.9, 135.7, 137.8, 139.6, 140.0, 141.1, 155.0, 155.4; HRMS (FAB-TOF) m/z calcd. for $C_{24}H_{22}N_2S$ 370.1504 [M$^+$], found 370.1520. Anal. Calcd for $C_{24}H_{22}N_2S$: C, 77.80; H, 5.99; N, 7.56. Found: C, 77.89; H, 5.99; N, 7.66.

Mixture of E/Z Isomers of 4-[2-{3-(10-methyl-10H-phenothiazinlyl)}vinyl][2.2]paracyclophane ***33***. To {3-(10-methyl-10*H*-

dx.doi.org/10.1021/jo5020273 | *J. Org. Chem.* 2014, 79, 11440−11453

phenothiazinyl)}methyltriphenylphosphonium bromide **30** (0.57 g, 1.00 mmol) in THF (5.0 mL) was added a 1.1 M THF solution of sodium hexamethyldisilazide (NaHMDS) (1.0 mL, 1.10 mmol) at 0 °C under an Ar atmosphere, and the mixture was continuously stirred at the same temperature for 30 min. 4-Formly[2.2]PCP **31** (0.12 g, 0.50 mmol) in THF (5.0 mL) was added to the mixture, and the mixture was stirred at room temperature for 3h. The reaction mixture was extracted with AcOEt, and the organic layer was dried with Na_2SO_4, filtered, the filtrate was concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography (hexane/CH_2Cl_2, 3/1, R_f = 0.15) to give 4-[2-{3-(10-methyl-10*H*-phenothiazinyl)}vinyl][2.2]-PCP **33** as yellow powder (0.16 g, 74%) as a *E*/*Z* mixture, which was used for the next reaction without separation of the *E*/*Z* isomers: mp 156−161 °C; HRMS (FAB-TOF) *m*/*z* calcd. for $C_{31}H_{27}NS$ 445.1864 [M^+], found 445.1876.

4-[2-{3-(10-Methyl-10H-phenothiazinlyl)}ethyl][2.2]paracyclophane ***25***. A *E*/*Z* mixture of 4-[2-{3-(10-methyl-10*H*-phenothiazinlyl)}vinyl][2.2]PCP **33** (45.1 mg, 0.10 mmol), 80% hydrazine monohydrate (0.31 mL, 5.0 mmol), and diethylene glycol (10 mL) was stirred at 100 °C for 1d. After cooling to room temperature, the reaction mixture was extracted with AcOEt. The organic layer was dried with Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2, 1/1, R_f = 0.64) and GPC with $CHCl_3$ to give 4-[2-{3-(10-methyl-10*H*-phenothiazinlyl)}ethyl][2.2]-PCP **25** as colorless solid (19.5 mg, 44%). Colorless solids (toluene and MeOH): mp 151−152 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.51 (m, 1H), 2.62 (t, *J* = 8.4 Hz, 2H), 2.80 (m, 2H), 2.99 (m, 6H), 3.33 (m, 1H), 3.37 (s, 3H), 6.16 (s, 1H), 6.39 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.44 (m, 3H), 6.51 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.64 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.93 (dd, *J* = 7.8, 0.6 Hz, 1H), 6.96 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 7.17 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.5, 34.3, 35.1, 35.3, 35.4, 36.0, 36.9, 114.0, 122.3, 123.3, 123.4, 127.0, 127.2, 127.3, 127.4, 128.9, 130.5, 132.1, 133.2, 133.3, 134.5, 134.8, 136.6, 137.4, 139.4, 139.8, 141.1, 143.9, 146.0; HRMS (FAB-TOF) *m*/*z* calcd. for $C_{31}H_{29}NS$ 447.2021 [M^+], found 447.2024. Anal. Calcd for $C_{31}H_{29}NS$: C, 83.18; H, 6.53; N, 3.13. Found: C, 83.32; H, 6.55; N, 3.15.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental methods, electrochemical properties, absorption and fluorescence spectral data, ^{1}H and ^{13}C NMR spectra, and theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

[¶]Donor−Bridge−Acceptor System 2. For part 1, see ref 1a.

■ ACKNOWLEDGMENTS

This work was supported by Management Express Grants for National Universities Cooperation from MEXT, Japan. We would like to thank Professors Tetsuro Majima and Mamoru Fujitsuka of The Institute of Scientific and Industrial Research (SANKEN), Okasa University, Japan, for strong collaboration. T.S. gratefully acknowledges the financial support for a Grant-in-Aid for Scientific Research (C) (No. 26410053) and a Grant-in-Aid for Scientific Research on Innovative Areas "Organic Synthesis based on Reaction Integration. Development of New Methods and Creation of New Substances" (No. 2105) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. T.M. is sincerely thankful for the financial support from the G-COE program, Science for Future Molecular Systems, Kyushu University, Japan. Computations were carried out using the computer facilities at the Research Institute for Information Technology, Kyushu University.

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(21) Cz-$(CH_2)_2$-[2.2]PCP-$(CH_2)_2$-NI **3** shows two oxidation potentials ($E^{ox}(I)$: +0.76 and +0.89 V), and the former is assigned as that of Cz, while the latter can be assigned as the oxidation potential due to the [3.3]PCP moiety because the first oxidation potential of Br$(CH_2)_3$-[3.3]PCP-$(CH_2)_3$-NI **16** ($E^{ox}(I)$: +0.91 and +1.26 V) is quite similar to that of **3**. Although **16** shows two oxidation potentials due to the [3.3]PCP moiety, **3** shows only one oxidation potential probably because the oxidation peak in **3** is too weak to measure.
(22) According to the reviewer's comment, we estimated the conformations of the exciplexes of the triads **1**−**3** based on the ground state calculations. The B3LYP/6-31G* optimized conformations of the stacked structures as exciplex models and the open-chain structures predicted that the relative stability of the stacked structure based on the open-chain one is comparable [+2.38 (**1**), +2.98 (**2**), and +2.35 kcal/mol (**3**)] (Scheme S15), but the calculations predict that **2** requires the largest energy for the formation of the stacked structure from the open-chain one. In the optimized stacked structures, the dihedral angle and the transannular distance between the NI π-face and the facing benzene ring of the cyclophane are estimated to be 5.4° (**1**), 8.9° (**2**), and 27.1° (**3**), as well as 4.5 (**1**), 4.4 (**2**), and 5.5 Å (**3**), respectively. These data indicate the more significant overlap and the shorter transannular distance of the π-faces in **1** and **2**, rather than **3**. Thus, the strong tendency of **2** to form the exciplex may be attributed to the stronger electron donating ability of the [3.3]PCP moiety than the [2.2]PCP moiety, and the higher flexibility of the trimethylene chain than the dimethylene one, which enables to take the stacked structure of the two π−faces with significant overlap. However, these data are based on the ground state calculations and the more detailed excited state calculations are required for the precise discussion on the exciplex structures.
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