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# Dynamic Molecular Tweezers Composed of Dibenzocyclooctatetraene Units: Synthesis, Properties, and Thermochromism in Host–Guest Complexes

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**Abstract:** Novel dynamic molecular tweezers (DMTs) **3a**, **3b**, **4a**, **4b**, and **5b**, composed of two tub-shaped dibenzocyclooctatetraene (DBCOT) units, were designed and synthesized. The cyclooctatetraene (COT) rings of these DMTs readily invert in solution, and the molecular structure shows rigid *syn* and *anti* forms in an equilibrium mixture in solution. The *syn* and *anti* conformers can be observed by NMR. The isomerization barriers of **3a**, **3b**, **4a**, **4b**, and **5b** are in the range of 16.5–21.3 kcal mol$^{-1}$, depending on steric repulsion between substituents of the COT rings and protons of the central benzene ring. These DMTs form complexes with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 1,2,4,5-tetracyano-benzene (TCNB) in solution and in the solid state. The binding abilities of these DMTs increase with electron-donating substituents on COT, which increase the electron densities of the cavity of the *syn* form, as supported by theoretical calculations. In addition, elongation of the terminal alkoxy chains of the DMTs was found to cause the enhancement of van der Waals contact with guest molecules. Therefore, **5b**, which has $CH_2OMe$ groups on the COT rings and longer ethoxy groups on the terminal benzene rings, showed the highest electron density of the cavity and hence the highest binding ability with the electron-deficient guest molecules. Interestingly, solutions of **3b**, **4b**, and **5b** show thermochromism in the presence of DDQ. A solution of **3b** or **4b** with DDQ in $CHCl_3$ is green due to charge-transfer interaction at room temperature and the color changes from green to yellow upon heating to 60 °C and from green to blue upon cooling to −40 °C, whereas the high complexation ability of **5b** with DDQ only shows a change in the shade of blue.

**Keywords:** cyclooctatetraene · density functional calculations · host–guest systems · molecular tweezers · thermochemistry

## Introduction

Belt-shaped conjugated systems have been attracting the attention of not only synthetic[1–3] but also theoretical chemists.[4] One of the most interesting properties of belt-shaped molecules is a host–guest interaction in supramolecular chemistry.[5] Because molecular belts have a preorganized and defined space inside the molecules, they function as a host molecule and form molecular complexes with a number of different guests.[6] Although cyclacenes, the basic belt-shaped units of $(n,0)$ carbon nanotubes,[7] have also been theoretically investigated and proposed as an interesting synthetic target,[8] no cyclacenes have been prepared to date, presumably due to their internal strain.[9]

As analogous systems, Gleiter and co-workers recently reported metal complexes of a belt-like molecule, $[4,8]_3$cyclacene (beltene)[10] and $[6.8]_3$cyclacene **1**.[11] In these molecules, tub-shaped cyclooctatetraene (COT) rings are fused with planar four- or six-membered rings. Thus, the internal strain of the beltene and **1** is small and hence beltene and **1** are stable in light and air.

Although the beltene and **1** have unique structures, the cavity of these molecules is too small to include any guest from a viewpoint of host–guest chemistry. In this regard, the cleft-shaped molecule **2**, which is a partial structure of **1** with two dibenzocyclooctatetraene (DBCOT) units, is interesting. Molecule **2** is considered to exist as an equilibrium mixture of *syn* and *anti* forms owing to ring inversion of

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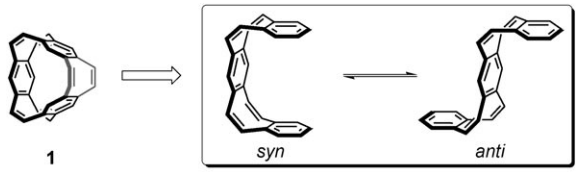


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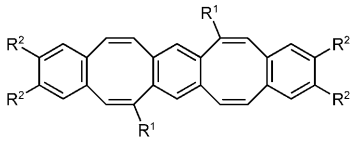
DBCOT ($\Delta G^{\neq} = 12$ kcal mol$^{-1}$).[12] Furthermore, because the face-to-face distance of the two terminal benzene rings in the *syn* form is calculated to be 6.6 Å in a preliminary model structure at the PM3 level, **2** can function as molecular tweezers to incorporate a planar guest between the two benzene rings.[13] With regard to molecular tweezers, Klärner's and Harmata's groups extensively investigated various systems with a rigid cleft structure,[14,15] whereas Fukazawa's group investigated flexible systems.[16] Unlike the presence of various stable conformations for Fukazawa's molecules, the most remarkable characteristic of the **2** molecular tweezers is that **2** takes only two conformers, i.e., the *syn* and *anti* forms. Among the two conformers, only the *syn* form functions as a molecular tweezers that interconvert with the *anti* form. Thus, **2** can act as a new host molecule for dynamic molecular recognition,[17] and it thus has potential for use as a molecular switch.[18]

Herein, we report the results of our investigations on the synthesis, structure, and unique binding behavior of dynamic molecular tweezers (DMTs) **3a**, **3b**, **4a**, **4b**, and **5b.** The



**3a**: $R^1$ = CN, $R^2$ = OMe
**3b**: $R^1$ = CN, $R^2$ = OEt
**4a**: $R^1$ = CHO, $R^2$ = OMe
**4b**: $R^1$ = CHO, $R^2$ = OEt
**5b**: $R^1$ = $CH_2OMe$, $R^2$ = OEt

binding abilities of these DMTs are strongly dependent on both substituents of the terminal benzene rings and two COT units. Furthermore, fine-tuning of the charge-transfer interaction of the DMTs and DDQ in $CHCl_3$ solutions has successfully led unique thermochromism.[19]

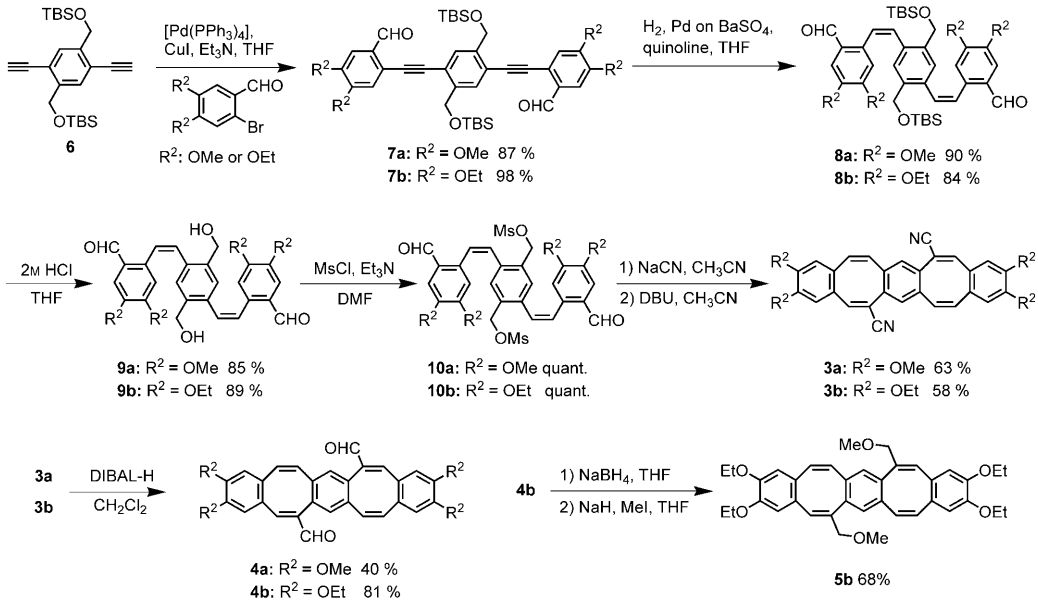
## Results and Discussion

**Synthesis of molecular tweezers 3a, 3b, 4a, 4b, and 5b**: The key step in the synthesis of these compounds is the formation of COT rings. Although a variety of simple methods for the preparation of COT and its derivatives have been reported,[20] we employed a stepwise pathway to construct COT rings of DMTs as shown in Scheme 1. The stepwise reactions enabled us to introduce substituent groups at the desired positions. First, **7a** and **7b** were prepared from **6** and two 2-bromo-4,5-dialkoxybenzaldehydes by the Sonogashira reaction. The two acetylene units of **7a** and **7b** were reduced to *cis* olefins by partial hydrogenation using Pd on $BaSO_4$ to afford **8a** and **8b**, respectively. Next, **10a** and **10b** were prepared by deprotection of the *tert*-butyldimethylsilyl groups in **8a** and **8b**, followed by mesylation of the hydroxyl groups in **9a** and **9b**. When **10a** and **10b** were reacted with NaCN, the formation of cyclized eight-membered ring compounds was observed by $^1$H NMR.[21] Therefore, a mixture of linear and cyclized compounds was used for the next condensation reaction by DBU without purification to produce molecular tweezers **3a** and **3b** in 63 and 58% yields from **10a** and **10b**, respectively. The dialdehydes **4a** and **4b** were synthesized by reduction of **3a** and **3b** using DIBAL-H to afford **4a** and **4b** in 40 and 81% yields, respectively. The low yield of **4a** is probably due to the low solubility of **3a**. The methoxymethyl derivative **5b** was obtained from **4b** in 68% yield.

**Structural properties of 3a, 3b, 4a, 4b, and 5b**: To estimate the relative energies ($E_{rel}$) of the *syn* and *anti* forms, optimization of the molecular structures of **3b**, **4b** and **5b** were performed at the B3LYP/6-31G(d) level[22] (Table 1). From the calculations, these $E_{rel}$ values are very small, and almost no difference in energy was observed between the *syn* and *anti* forms. In the $^1$H NMR spectra of DMTs at room temperature, both *syn* and *anti* forms were observed independently. As shown in Table 1, the observed differences in free energy ($\Delta G°$) between *syn* and *anti* isomers are small ($<1$ kcal mol$^{-1}$), but slightly larger than the calculated results. On the NMR timescale, exchange rates of *syn* and *anti* isomers of these DMTs are slow at room temperature owing to steric repulsion between COT substituents and protons of the central benzene ring. Therefore, we performed VT $^1$H NMR and determined the isomerization barriers of these DMTs. Although both *syn* and *anti* forms of **3b** were observed at 30°C (Figure 1), the signals of the *syn* and *anti* forms gradually coalesced to give signals assigned as the molecule with an apparent $C_2$ symmetry at higher temperatures. As shown in Table 2, the isomerization barriers ($\Delta G^{\neq}$) of **3a** and **3b** are 16.5 kcal mol$^{-1}$, whereas the barriers of **4a**, **4b**, and **5b** are approximately 21.0 kcal mol$^{-1}$. These results indicate that the steric repulsion of the CN group is smaller than that of the CHO and $CH_2OMe$ groups due to the linear structure of the CN group. In addition, the theoretical calculations for the inversion barriers ($\Delta E$) of **3′**, **4′**, and **5′**, which were estimated by the energy difference between the tub and planar structures, gave values (**3′**: 14.1, **4′**: 20.1, **5′**: 20.6 kcal mol$^{-1}$) similar to the observed inversion barriers of **3a**, **3b**, **4a**, **4b**, and **5b**.

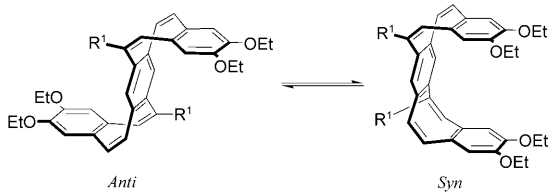
Among these DMTs, single crystals of **4a** were obtained from DMF, and the crystal structure of **4a**·2DMF was determined by X-ray analysis (Figure 2). Although the *syn* form of **4a** is slightly more stable than the *anti* form of **4a** in DMF solution, **4a** takes the *anti* form in the solid state. The dihedral angle between the central and terminal benzene




Scheme 1. Synthesis of dynamic molecular tweezers **3a**, **3b**, **4a**, **4b**, and **5b**.

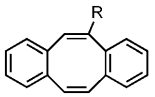
Table 1. Calculated relative energies ($E^{rel}$)[a] and observed free energies ($\Delta G°$)[b] of *anti* and *syn* isomers of **3b**, **4b**, and **5b**.




| | $E_{rel}$ [kcal mol$^{-1}$] | | $\Delta G°$ [kcal mol$^{-1}$] | |
|---|---|---|---|---|
| | *anti* | *syn* | *anti* | *syn* |
| **3b**: $R^1$ = CN | 0.00 | 0.08 | 0.00 | 0.59 |
| **4b**: $R^1$ = CHO | 0.06 | 0.00 | 0.89 | 0.00 |
| **5b**: $R^1$ = $CH_2OMe$ | 0.00 | 0.02 | 0.00 | 0.39 |

[a] Calculated at the B3LYP/6-31G(d) level. [b] Determined by $^1$H NMR measurements in $CDCl_3$.

Table 2. Isomerization barriers ($\Delta G^{\neq}$) and coalescence temperatures ($T_C$) of **3a**, **3b**, **4a**, **4b**, and **5b**, and calculated inversion barriers ($\Delta E^{\neq}$) of DBCOT derivatives of **3′**, **4′**, and **5′**.



**3′**: R = CN
**4′**: R = CHO
**5′**: R = $CH_2OMe$

| | $\Delta G^{\neq}$ [kcal mol$^{-1}$] | $T_C$ [°C] | $\Delta E^{\neq}$ [kcal mol$^{-1}$] |
|---|---|---|---|
| **3a** | 16.5 | 50 | – |
| **3b** | 16.5 | 50 | – |
| **3′** | – | – | 14.1 |
| **4a** | 21.2 | 135 | – |
| **4b** | 20.8 | 130 | – |
| **4′** | – | – | 20.1 |

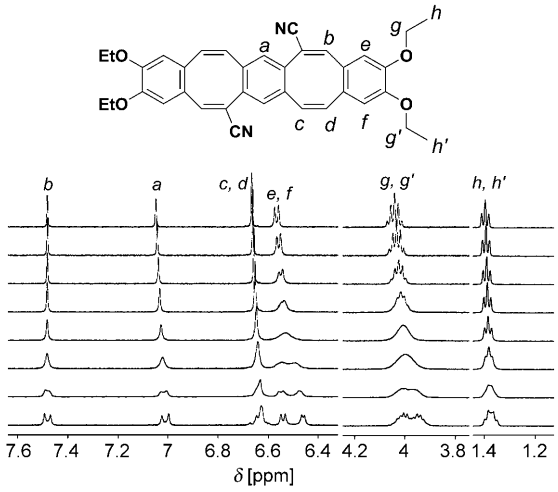



Figure 1. VT $^1$H NMR spectra of **3b** (500 MHz in $CDCl_2CDCl_2$).

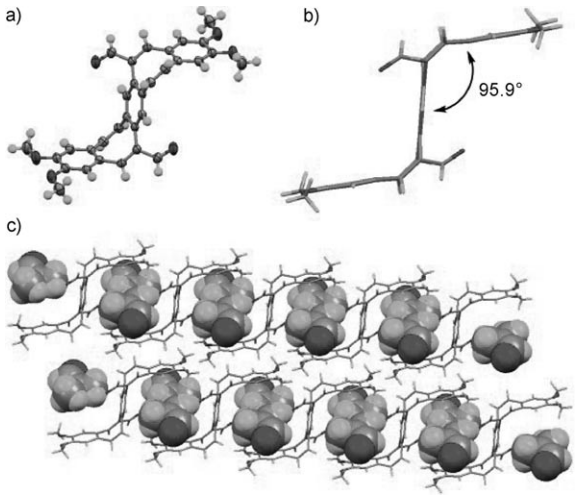



Figure 2. Crystal structures of **4a**: a) ellipsoid drawing, b) side view, c) packing structures of **4a** (wireframe) with DMF (CPK model).

rings is 95.9°, which is slightly narrower than in the case of the parent DBCOT (99°).[23] As shown in Figure 2c, DMF was incorporated in the cavity formed by two adjacent **4a** molecules.

**Binding properties of DMTs**: The binding abilities and behaviors of DMTs **3**–**5** with various π acceptors were investigated by analyzing UV/Vis and $^1$H NMR spectra. Among π acceptors, these DMTs formed host–guest complexes in solution with 1,2,4,5-tetracyanobenzene (TCNB), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 1,3,5-trinitrobenzene (TNB), whereas no complexation was observed with other small acceptors such as 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), TCNQ-$F_4$, pyridinium salts, and viologen. In particular, the CT interaction between these DMTs and DDQ caused a color change from green to blue. The UV/Vis titration of **3b** with DDQ is shown in Figure 3. The CT

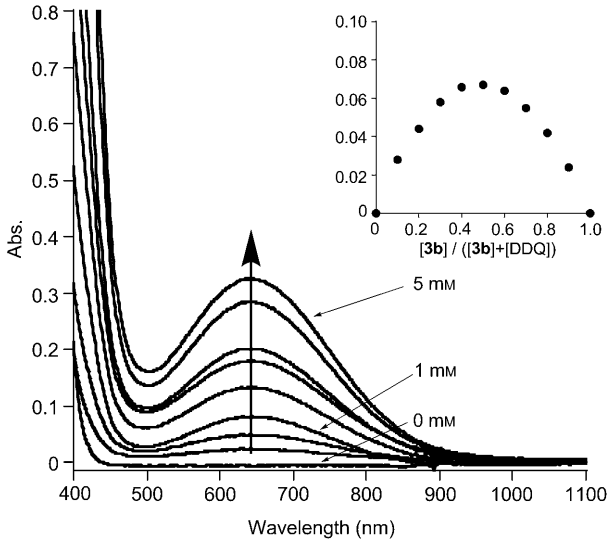



Figure 3. UV/Vis titration of **3b** with DDQ (**3b**: 0.5 mM). The concentrations of DDQ used are (from bottom to top) 0.0, 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 4.0, 5.0 mM. The insert is a Job's plot ([**3b**] + [DDQ] = 1.0 mM) at 640 nm (solvent: $CHCl_3$).

absorption of **3b** with DDQ appeared at 640 nm (Figure 3a), and Job's plot ([**3b**] + [DDQ] = 1.0 mM) at 640 nm indicates the formation of a 1:1 complex (Figure 3b).

The $^1$H NMR titration experiments are also useful for investigating the binding behavior and binding constants of DMTs. The experiment of **3b** with DDQ is shown in Figure 4 as a representative result. Although no shift of the *anti* protons was observed as the concentration of DDQ increased, the *syn* protons gradually shifted to either the upper or lower field. The complexation-induced shift (CIS) of the terminal benzene protons $H_e$ and $H_f$ is 0.28 ppm, and the relative intensities of the *syn* peaks gradually increased. These results indicate that the equilibrium is shifted toward the *syn* isomer by the addition of DDQ and that only the *syn* isomer forms the 1:1 complex with DDQ.

Table 3 summarizes the binding constants $K_C$ of DMTs with TCNB, DDQ, or 1,3,5-trinitrobenzene (TNB)[24] together with thermodynamic parameters $\Delta H_{DDQ}$ and $\Delta S_{DDQ}$ of the complexation with DDQ. Irrespective of slight structural differences among DMTs **3a**, **3b**, **4a**, **4b**, and **5b**, the binding constants were increased by elongation of terminal alkoxy chains from OMe to OEt groups and by increasing the electron-donating ability of COT substituents from CN, CHO to $CH_2OMe$ groups. Thus **5b** has the highest binding constants.

The $\Delta H_{DDQ}$ of **3b** and **4b** , which have OEt groups, shows more favorable binding with DDQ by 1.2–1.4 kcal mol$^{-1}$ compared to the binding of **3a** and **4a**, which have OMe groups. On the other hand, the $\Delta S_{DDQ}$ terms for **3b** and **4b** are less favorable than those of **3a** and **4a** by 0.7 and 1.6 eu, respectively. These results indicate that the van der Waals interaction between terminal alkoxy chains of DMTs and DDQ was increased by the elongation of the chains from OMe to OEt, whereas increased flexibilities of these alkoxy chains resulted in the negatively larger $\Delta S_{DDQ}$ terms. Moreover, the $\Delta H_{DDQ}$ values of **4a** and **4b**, which have CHO groups, show more favorable binding with DDQ than those of **3a** and **3b**, which have CN groups, by about 1.0 kcal mol$^{-1}$, and also **5b** , which has $CH_2OMe$ groups, shows more favorable binding with DDQ than **4b** by about 1.7 kcal mol$^{-1}$. From these results, we thought COT substituents of CN, CHO, and $CH_2OMe$ were likely to affect the electron densities of the binding sites in DMTs.

In order to estimate the electrostatic effect on the binding of DMTs with guest molecules, we optimized the structures of the *syn* form (B3LYP/6-31G* level) and calculated the electrostatic potential surfaces (ESPs) of **3b**, **4b**, and **5b** (Figure 5). From these ESPs, the electron densities of the cavities of **3b**, **4b**, and **5b** show marked differences, and the negative character of the central and terminal benzene rings increases in the order of **3b** < **4b** < **5b**. Therefore, it is clear that these differences in ESP affect the binding ability ($\Delta H$) with electron-deficient guest molecules. This electrostatic effect of substituents on COT units efficiently extended into whole molecules, indicating that the COT units are effectively conjugated with the central and terminal benzene rings, in spite of the bending π systems.

On the other hand, the $\Delta S_{DDQ}$ values of **3b**, **4b**, and **5b** decrease in the order of **3b** > **4b** > **5b**. If *syn* forms of the DMTs have the preorganization effect[25] derived from the cavity sizes, $\Delta S_{DDQ}$ values have to increase in the order of **3b** < **4b** < **5b** because the cavity sizes of DMTs (the distance between both terminal oxygen atoms from theoretical calculation) decrease in the order of **3b** (9.293 Å) > **4b** (9.147 Å) > **5b** (8.631 Å). Therefore, in this case, the preorganization effect caused by the cavity sizes seems not to be important and flexibilities of the COT substituents are considered to be a more effective factor in the $\Delta S_{DDQ}$ terms. This can be rationalized by decreasing the flexibilities of COT substituents upon complexation with guest molecules.

The structures of the complexes of TCNB@**4b** and TCNB@**5b** were determined by X-ray crystallography and

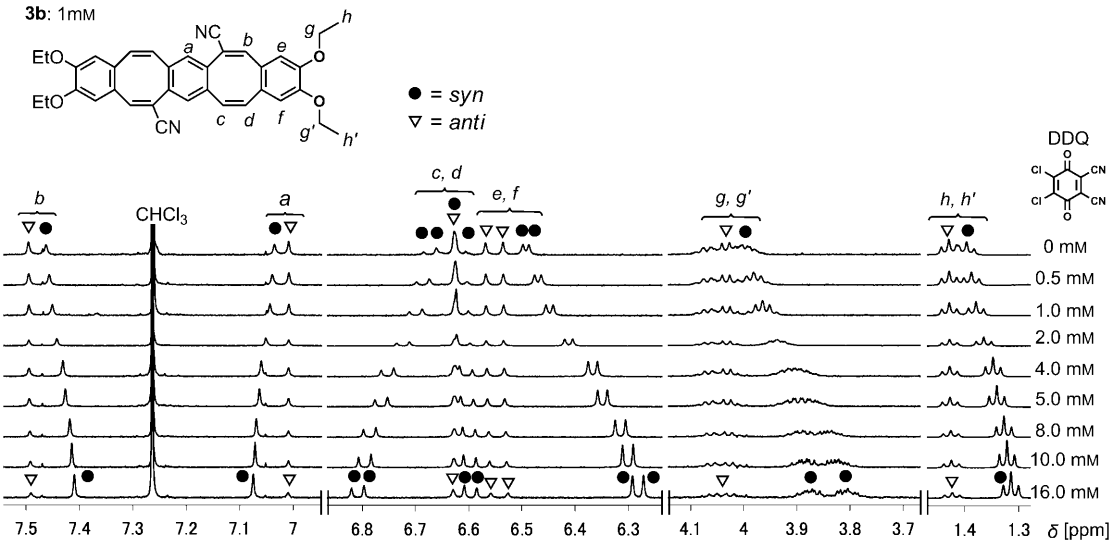



Figure 4. The NMR titration of **3b** with DDQ (**3b**: 1 mM, solvent: $CDCl_3$).

Table 3. Binding constants of $K_C$ [$M^{-1}$] of DMTs with TCNB, DDQ, or TNB together with thermodynamic parameters of $\Delta H_{DDQ}$ [kcal $mol^{-1}$] and $\Delta S_{DDQ}$ [cal $mol^{-1} K^{-1}$] of DDQ complex.[24]

| Substrate | **3a** | **3b** | **4a** | **4b** | **5b** |
|---|---|---|---|---|---|
| TCNB | <300 | 530 | 730 | 1100 | 10000[a] |
| DDQ | 40 | 240 | 70 | 360 | 1570 |
| TNB | –[b] | –[b] | –[b] | 28 | 35 |
| $\Delta H_{DDQ}$ | −2.4 | −3.6 | −3.2 | −4.6 | −6.3 |
| $\Delta S_{DDQ}$ | −0.8 | −1.5 | −2.4 | −4.0 | −7.0 |

[a] Determined by UV/Vis titration (solvent: $CHCl_3$). [b] The $K_C$ value could not be determine because the interaction was very weak.

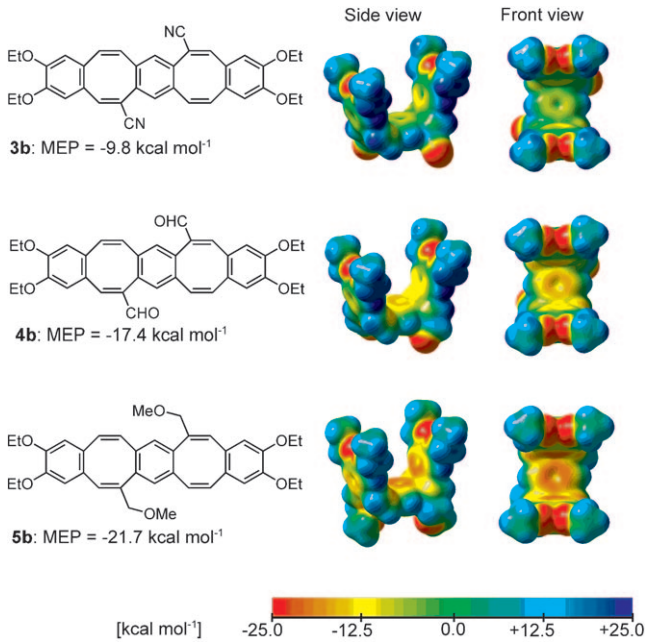



Figure 5. Electrostatic potential surfaces and the values of molecular electrostatic potentials (MEPs, calculated position of MEP is 2.0 Å above the central benzene ring) of **3b**, **4b**, and **5b** (B3LYP/6-31G*//B3LYP/6-31G*).

the results of TCNB@**4b** are shown in Figure 6. As shown in Figure 6b, TCNB and terminal benzene rings stack through π–π interactions at a distance of 3.33–3.40 Å, and the dihedral angles between terminal and central benzene rings in **4b** are about 90°. Moreover, the distance between the proton of TCNB and the central benzene ring of **4b** is 2.54 Å, indicating the presence of a CH–π interaction (Figure 6c). The CH–π interaction would result in improved binding of TCNB than DDQ, in spite of it being the weaker acceptor. In the packing structure, two complexes stack through π–π interactions, and the chloroform molecules from the recrystallizing solvent are located on the opposite side of the TCNB (Figure 6d). The terminal ethoxy groups

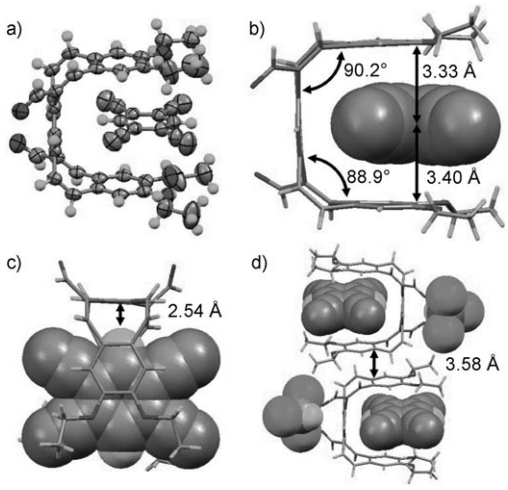



Figure 6. Crystal structures of TCNB@**4b**: a) ellipsoid drawing, b) side view, c) top view, d) packing structures.

of **4b** were found to cover the guest molecule of TCNB, suggesting that the ethoxy chains play an important role in the binding of the guest molecule as observed in the binding study.

Although many molecular tweezers have been reported, most studies focus on the relationship between the π plane area of recognition sites and the binding ability because compounds with a rigid and wide π plane readily interact with many electron-deficient molecules by π–π and/or CT interactions. From this point of view, our synthesized DMTs show unique molecular recognition by means of not only π–π, CH–π, and CT interactions, but also by van der Waals interactions between flexible alkoxy chains.

**Thermochromic properties of DDQ@DMT complexes**: Although **3b** and **4b** have a lower binding ability than **5b** owing to electron-withdrawing substituents on the COT units, it is interesting that these solutions of DDQ complexes exhibit thermochromic properties. Figure 7 shows solutions of **3b**, **4b**, and **5b** with DDQ in $CHCl_3$ at various temperatures.

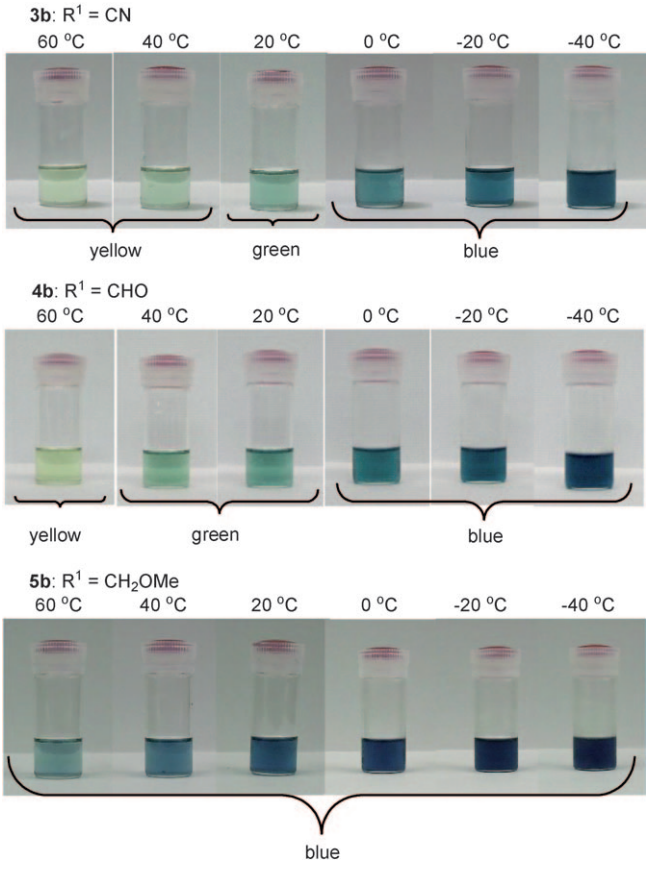



Figure 7. Solutions of **3b**, **4b**, and **5b** with DDQ in $CHCl_3$ (DDQ: 1 mM, DMTs: 1 mM) at variable temperatures (60 to −40°C).

The solutions of **3b** and **4b** with DDQ in $CHCl_3$ are green at room temperature. However, the color gradually changes from green to yellow upon heating to 60°C and from green to blue upon cooling to −40°C. On the other hand, **5b** with DDQ only shows a change in the shade of blue. This thermochromism has a good response to changes in temperature. A $CHCl_3$ solution of DDQ is yellow and that of the DDQ@DMT complex is blue. Therefore, the principle of this thermochromism is related to the mixing ratio of yellow and blue; the color is decided by the molar ratio of the DDQ@DMT complex to free DDQ. Table 4 shows the molar ratio of DDQ@**3b**, DDQ@**4b**, and DDQ@**5b** complexes to free DDQ ([DDQ@DMTs]/[DDQ]) in $CHCl_3$ at temperatures between 60°C and −40°C.

Table 4. The ratio of [DDQ@DMTs]/[DDQ] (DDQ: 1 mM, DMTs: 1 mM) in $CHCl_3$ solutions calculated by means of a van't Hoff plot.[26]

| $T$ [°C] | [DDQ@**3b**]/[DDQ] | [DDQ@**4b**]/[DDQ] | [DDQ@**5b**]/[DDQ] |
|---|---|---|---|
| 60 | 0.10 | 0.12 | 0.31 |
| 40 | 0.14 | 0.18 | 0.50 |
| 20 | 0.20 | 0.28 | 0.85 |
| 0 | 0.30 | 0.45 | 1.39 |
| −20 | 0.46 | 0.74 | 2.34 |
| −40 | 0.70 | 1.24 | 4.61 |

As shown in Figure 7 and Table 4, the solution was yellow at a ratio below 0.14, green at a ratio range of 0.18 to 0.28, and blue at a ratio over 0.30. From these results, the COT substituents adequately tuned not only the binding ability but also the thermochromism.

The CT bands of the complexes of **3b** (640 nm), **4b** (655 nm), and **5b** (680 nm) with DDQ at 20°C showed red-shifts according to the donating ability of the substituents on the COT rings. These results are consistent with Mulliken charge–transfer theory,[27] namely, $h\nu_{CT} = IP - EA - e_0^2/\varepsilon r$, where $IP$, $EA$, and $e_0^2/\varepsilon r$ denote the first ionization energy of the donor, the electron affinity of the acceptor, and the electrostatic work term, respectively, where $\varepsilon$ is the dielectric constant of the solvent, and $r$ is the plane-to-plane distance between donor and acceptor.[28] On the other hand, as shown in Figure 8, the absorption maxima of the CT band

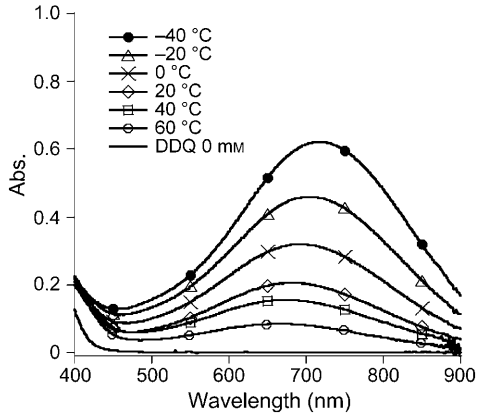



Figure 8. VT UV/Vis spectra of **5b** with DDQ (**5b**: 0.5 mM, DDQ: 0.5 mM, $CHCl_3$) at 60°C to −40°C.

of **5b** in DDQ solution shifted to a longer wavelength from 665 to 715 nm with decreasing temperature. Similar redshifts were also observed in the case of **3b** (630→680 nm) and **4b** (635→690 nm). The reason for this redshift is not clear. One possible explanation could be a reduction in the distance between DDQ and the terminal aromatic rings of DMTs due to suppression of the thermal vibrations of the complex, which may affect the electrostatic work term ($e_0^2/\varepsilon r$). Irrespective of the presence of redshifts in the CT bands, these CT absorptions cause a similar blue color.

## Conclusions

In summary, we synthesized novel dynamic molecular tweezers **3a**, **3b**, **4a**, **4b**, and **5b** composed of two DBCOT units. These DMTs form an equilibrium mixture of *anti* and *syn* isomers in solution and these isomers were observed independently in NMR spectra at room temperature. The isomerization barriers of the *anti* and *syn* forms depend on the bulkiness of the COT substituents. From the investigations of binding behavior of DMTs, only the *syn* form could interact with guest molecules such as DDQ and TCNB, and the electron-donating substituents on the COT rings and elongation of terminal alkoxy groups were found to enhance the binding abilities. In particular, in spite of **3b** and **4b** having a lower binding ability than **5b**, both DDQ@**3b** and DDQ@**4b** solutions show clear thermochromism from yellow to green and green to blue, depending on the molar ratio of [DDQ@DMTs]/[DDQ]. The unique thermochromism mechanism owes principally to dynamic molecular recognition, and, to our knowledge, this type of thermochromism has not been previously reported.

## Experimental Section

**General**: $^1$H NMR and $^{13}$C NMR spectra were recorded on a JEOL LA-500 instrument ($^1$H: 500 MHz; $^{13}$C{$^1$H}: 125 MHz) at 23 °C unless stated otherwise. Chemical shift values are given in $\delta$ (ppm) relative to internal $SiMe_4$ or residual solvent. Mass spectra were recorded on SHIMADZU GCMS-QP2010 and KRATOS AXIMA-CFR instruments. Only the more intense or structurally diagnostic mass spectral fragment ion peaks are reported. Electronic spectra were recorded on a SHIMADZU UV-VIS-NIR scanning spectrophotometer (Model UV-3101-PC). Melting points were determined with a Yanaco MP-500D melting point apparatus. Elemental analyses were performed in the microanalysis laboratory of Tokyo Metropolitan University. Column chromatography was carried out on Merck silica gel 60, 70–230 mesh ASTM, and Daiso silica gel 1001W. All solvents were dried by conventional procedures and distilled before use. DDQ was purified by column chromatography on silica gel with $CHCl_3$/EtOAc (v/v = 10:1) and recrystallized from $CHCl_3$. Commercially available TNB was dissolved in $CH_2Cl_2$ and dried with $MgSO_4$. All other commercially available materials were of reagent grade, unless stated otherwise.

**Computational methods**: All calculations were conducted with Gaussian 03 programs. The geometries were optimized with the restricted Becke hybrid (B3LYP) at the 6-31G(d) level.

**Bis-1,4-(*tert*-butyldimethylsiloxymethyl)-bis-2,5-(2′-formyl-4′,5′-dimethoxyphenyl-ethynyl)benzene (7a)**: A mixture of **6**[29] (6.22 g, 15.0 mmol), 2-bromo-4,5-dimethoxybenzaldehyde (7.72 g, 31.5 mmol), [Pd(PPh$_3$)$_4$] (345 mg, 0.3 mmol), and CuI (114 mg, 0.6 mmol) in $Et_3N$ (150 mL) was stirred for 1 h under an argon atmosphere at 75 °C. A mixture of $CHCl_3$ and aq. $NH_4Cl$ solution was added into the reaction mixture, which was then separated. The organic layer was washed with 2 M HCl, water, and brine and then dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, benzene). Recrystallization from ether/hexane gave **7a**. Yield: 9.70 g, 13.05 mmol (87.0 %); yellow crystals; m.p. 208–209 °C; MS (LDI-TOF): *m/z*: 742 $[M]^+$; $^1$H NMR ($CDCl_3$): $\delta$ = 10.50 (s, 2H), 7.70 (s, 2H), 7.45 (s, 2H),7.05 (s, 2H), 4.96 (s, 4H), 4.01 (s, 6H), 3.98 (s, 6H), 0.98 (s, 18H), 0.16 ppm (s, 12H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 190.0, 153.6, 150.0, 141.8, 130.2, 129.7, 121.2, 120.1, 114.3, 108.3, 92.4, 91.3, 63.2, 56.3, 56.2, 26.0, 18.5, −5.2 ppm; elemental analysis calcd (%) for $C_{42}H_{54}O_8Si_2$: C 67.89, H 7.33; found: C 67.70, H 7.19.

**Bis-1,4-(*tert*-butyldimethylsiloxymethyl)-bis-2,5-(2′-formyl-4′,5′-diethoxyphenyl-ethynyl)benzene (7b)**: Compound **7b** was prepared by a procedure similar to that used for **7a**. Yield: 11.7 g, 14.7 mmol, 98.0 %; yellow crystals; m.p. 180–182 °C; MS (LDI-TOF): *m/z*: 798 $[M]^+$; $^1$H NMR ($CDCl_3$): $\delta$ = 10.47 (s, 2H), 7.69 (s, 2H), 7.43 (s, 2H),7.03 (s, 2H), 4.95 (s, 4H), 4.22 (q, *J* = 7.0 Hz, 4H), 4.20 (q, *J* = 7.0 Hz, 4H), 1.53 ( t, *J* = 7.0 Hz, 3H), 1.50 ( t, *J* = 7.0 Hz, 3H), 0.97 (s, 18H), 0.15 ppm (s, 12H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 190.0, 153.3, 149.5, 141.8, 129.9, 129.6, 120.9, 120.1, 115.4, 109.5, 92.2, 91.4, 64.8, 64.6, 63.1, 26.0, 18.5, 14.5, −5.2 ppm; elemental analysis calcd (%) for $C_{46}H_{62}O_8Si_2$: C 69.13, H 7.82; found: C 69.09; H 7.82.

**Bis-1,4-(*tert*-butyldimethylsiloxymethyl)-bis-2,5-(2′-formyl-4′,5′-dimethoxyphenyl-ethenyl)benzene (8a)**: A mixture of **7a** (0.74 g, 1.0 mmol), Pd on $BaSO_4$ (0.5 g), and quinoline (1 mL) in THF (25 mL) was stirred for 3 h at room temperature under an $H_2$ atmosphere. After Pd on $BaSO_4$ was removed by filtration, the solution was concentrated. The residue was dissolved in $CH_2Cl_2$, washed with 2 M HCl and water, and dried over magnesium sulfate. After evaporation of solvent, the residue was purified by column chromatography (silica gel, $CHCl_3$). Recrystallization from $CH_2Cl_2$/hexane gave **8a**. Yield: 0.67 g, 0.89 mmol (89.7 %); yellow crystals; m.p. 172–173 °C; MS (EI): *m/z*: 746 $[M]^+$; $^1$H NMR ($CDCl_3$): $\delta$ = 10.15 (s, 2H), 7.31 (s, 2H), 7.08 (d, *J* = 12.2 Hz, 2H),7.06 (s, 1H), 6.84 (d, *J* = 11.9 Hz, 2H), 6.55 (s, 2H), 4.48 (s, 4H), 3.90 (s, 6H), 3.57 (s, 6H), 0.80 (s, 18H), −0.07 ppm (s, 12H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 189.9, 153.3, 148.5, 137.8, 135.2, 133.4, 130.8, 128.2, 126.63, 126.60, 112.4, 109.7 , 62.8, 55.9, 55.9, 25.8, 18.2, −5.6 ppm; elemental analysis calcd (%) for $C_{42}H_{58}O_8Si_2$: C 67.52, H 7.83; found: C 67.46, H 7.81.

**Bis-1,4-(*tert*-butyldimethylsiloxymethyl)-bis-2,5-(2′-formyl-4′,5′-diethoxyphenyl-ethenyl)benzene (8b)**: Compound **8b** was prepared by a procedure similar to that used for **8a**. Yield: 1.35 g, 1.68 mmol, 84.0 %; yellow crystals; m.p. 130–131 °C; MS (EI): *m/z*: 802 $[M]^+$; $^1$H NMR ($CDCl_3$): $\delta$ = 10.15 (s, 2H), 7.30 (s, 2H), 7.09 (d, *J* = 12.2 Hz, 2H),7.04 (s, 2H), 6.80 (d, *J* = 12.2 Hz, 2H), 6.50 (s, 2H), 4.47 (s, 4H), 4.11 (q, *J* = 7.0 Hz, 4H), 3.74 (q, *J* = 7.0 Hz, 4H), 1.45 (t, *J* = 7.0 Hz, 6H), 1.22 (t, *J* = 7.0 Hz, 6H), 0.80 (s, 18H), −0.07 ppm (s, 12H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 190.0, 152.8, 148.0, 137.7, 134.8, 133.5, 130.5, 128.1, 127.0, 126.4, 113.6 111.2 , 64.23, 64.16, 62.8, 25.8, 18.2, 14.6, 14.2, −5.6 ppm; elemental analysis calcd (%) for $C_{46}H_{66}O_8Si_2$: C 68.79, H 8.28; found: C 68.75, H 8.30.

**Bis-1,4-(2′-formyl-4′,5′-dimethoxyphenylethenyl)-bis-2,5-(hydroxymethyl)-benzene (9a)**: A solution of **8a** (3.74 g, 5.0 mmol) and 2 M HCl (20 mL) in THF (100 mL) was stirred for 1 h at room temperature, and then hexane (200 mL) was added. The resulting white precipitate (**9a**) was filtered and rinsed with EtOH and ether to give **9a**. Yield: 2.20 g, 4.24 mmol (84.8 %); white powder; m.p. 221–223 °C; MS (EI): *m/z*: 518 $[M]^+$; $^1$H NMR ([D$_6$]DMSO): $\delta$ = 10.05 (s, 2H), 7.28 (s, 2H), 7.16 (d, *J* = 12.2 Hz, 2H),7.00 (s, 1H), 6.88 (d, *J* = 11.9 Hz, 2H), 6.67 (s, 2H), 4.97 (t, *J* = 5.2 Hz, 2H), 4.26 (d, *J* = 5.2 Hz, 4H), 3.79 (s, 6H), 3.46 ppm (s, 6H); $^{13}$C NMR ([D$_6$]DMSO): $\delta$ = 190.3, 152.9, 148.1, 138.4, 134.6, 133.4, 130.6, 127.9, 126.9, 126.2, 112.5, 110.2, 60.5, 55.45, 55.41 ppm; elemental analysis calcd (%) for $C_{30}H_{30}O_8$: C 69.49, H 5.83; found: C 69.48, H 5.94.

**Bis-1,4-(2′-formyl-4′,5′-diethoxyphenylethenyl)-bis-2,5-(hydroxymethyl)-benzene (9b)**: Compound **9b** was prepared by a procedure similar to that used for **9a**. Yield: 2.04 g, 3.56 mmol, 88.9 %; yellow powder; m.p. 183–

184 °C; MS (EI): *m/z*: 574 $[M]^+$; $^1$H NMR ([D$_6$]DMSO): $\delta$ = 10.03 (s, 2H), 7.25 (s, 2H), 7.14 (d, $J$ = 11.9 Hz, 2H), 6.99 (s, 2H), 6.84 (d, $J$ = 11.9 Hz, 2H), 6.64 (s, 2H), 4.96 (t, $J$ = 5.2 Hz, 2H), 4.24 (d, $J$ = 5.2 Hz, 4H), 4.03 (q, $J$ = 7.0 Hz, 4H), 3.71 (q, $J$ = 7.0 Hz, 4H), 1.31 (t, $J$ = 7.0 Hz, 6H), 1.11 ppm (t, $J$ = 7.0 Hz, 6H); $^{13}$C NMR ([D$_6$]DMSO) $\delta$ = 190.4, 152.2, 147.3, 138.3, 134.3, 133.4, 130.3, 127.8, 127.0, 126.0, 113.4, 111.5, 63.7, 63.7, 60.5, 14.6, 14.1 ppm; elemental analysis calcd (%) for $C_{30}H_{30}O_8$: C 71.06, H 6.67; found: C 71.03, H 6.80.

**Bis-1,4-(2′-formyl-4′,5′-dimethoxyphenylethenyl)-bis-2,5-(methanesulfonyl-methyl)benzene (10a)**: To a solution of **9a** (1.04 g, 2.0 mmol) and $Et_3N$ (1.66 mL, 12.0 mmol) in DMF (100 mL) was added methanesulfonyl chloride (0.46 mL, 6.0 mmol) dropwise at −55 °C under an $N_2$ atmosphere. The solution was stirred for 15 min at the same temperature. The reaction was quenched by addition of aqueous saturated $NaHCO_3$, and the mixture was extracted with $CHCl_3$. The organic layer was washed with 2 M HCl, water, and brine, and then dried over magnesium sulfate. The solvent volume was reduced to $^1/_5$ by evaporation. The resulting yellow precipitate (**10a**) was filtered and rinsed with hexane to give **10a**. Yield: 1.35 g, 2.0 mmol, (100 %); yellow crystals; m.p. 171–172 °C (decomp); MS (EI): *m/z*: 674 $[M]^+$; $^1$H NMR ($CDCl_3$): $\delta$ = 10.06 (s, 2H), 7.31 (s, 2H), 7.22 (d, $J$ = 12.25 Hz, 2H),7.01 (s, 2H), 6.87 (d, $J$ = 11.9 Hz, 2H), 6.53 (s, 2H), 4.98 (s, 4H), 3.92 (s, 6H), 3.66 (s, 6H), 2.88 ppm (s, 6H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 190.1, 153.7, 149.0, 135.9, 134.2, 132.8, 132.0, 130.3, 128.8, 126.9, 112.4, 110.8, 68.1, 56.3, 56.2, 37.9 ppm; HR-MS (EI): *m/z*: calcd for $C_{32}H_{34}O_{12}S_2$ $[M]^+$: 674.1491; found: 674.1570.

**Bis-1,4-(2′-formyl-4′,5′-diethoxyphenylethenyl)-bis-2,5-(methanesulfonyl-methyl)benzene (10b)**: **10b** was prepared by a procedure similar to that used for **10a**. Yield: 2.53 g, 3.46 mmol 100 %; yellow crystals; m.p. 156–158 °C (decomp); MS (EI): *m/z*: 730 $[M]^+$; $^1$H NMR ($CDCl_3$): $\delta$ = 10.05 (s, 2H), 7.30 (s, 2H), 7.22 (d, $J$ = 11.9 Hz, 2H), 6.99 (s, 2H), 6.83 (d, $J$ = 11.9 Hz, 2H), 6.48 (s, 2H), 4.96 (s, 4H), 4.13 (q, $J$ = 7.0 Hz, 4H), 3.83 (q, $J$ = 7.0 Hz, 4H), 2.88 (s, 6H), 1.46 (t, $J$ = 7.0 Hz, 6H), 1.30 ppm (t, $J$ = 7.0 Hz, 6H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 190.0, 153.1, 148.3, 135.8, 133.7, 132.6, 131.8, 130.4, 128.3, 126.5, 113.3, 112.2, 68.1, 64.5, 64.5, 37.7, 14.6, 14.3 ppm; elemental analysis calcd (%) for $C_{36}H_{42}O_{12}S_2$ :C 59.16, H 5.79; found: C 58.90, H 5.79.

**Molecular tweezers 3a**: To a solution of **10a** (628 mg, 0.93 mmol) in MeCN (140 mL) was added NaCN (147 mg, 3.0 mmol) in DMF (60 mL) dropwise at room temperature under an $N_2$ atmosphere. After stirring for 2 h, the reaction was quenched by addition of 2 M aqueous HCl and extracted with $CHCl_3$. The organic layer was washed with water and brine, and then dried over magnesium sulfate. After evaporation of the solvent, the residue was dissolved in MeCN (100 mL), and DBU (1 mL) was added at 110 °C under an $N_2$ atmosphere. The mixture was stirred for 1 h. The resulting white precipitate (**3a**) was filtered and rinsed with EtOH and ether to give **3a**. Yield: 291 mg, 0.58 mmol (62.5 %); white powder; m.p. 308–310 °C (decomp); MS (LDI-TOF): *m/z*: 500 $[M]^+$; $^1$H NMR ($C_2D_2Cl_4$ 90 °C): $\delta$ = 7.50 (s, 2H), 7.06 (s, 2H), 6.68 (s, 4H), 6.57 (s, 2H), 6.55 (s, 2H), 3.83 (s, 6H), 3.81 ppm (s, 6H); $^{13}$C NMR ($C_2D_2Cl_4$ 90 °C): $\delta$ = 153.4, 152.1, 151.7, 140.5, 136.9, 136.5, 133.9, 133.3, 132.8, 128.9, 122.7, 118.9, 116.0, 115.3, 59.3, 59.1 ppm; elemental analysis calcd (%) for $C_{32}H_{24}N_2O_4$: C 76.78, H 4.83; N, 5.60; found: C76.77, H 4.70; N, 5.68.

**Molecular tweezers 3b**: Compound **3b** was prepared by a procedure similar to that used for **3a**. Yield: 343 mg, 0.580 mmol, 58.3 %; white powder; m.p. 260–262 °C (decomp); MS (LDI-TOF): *m/z*: 556 $[M]^+$; $^1$H NMR ($C_2D_2Cl_4$, 90 °C): $\delta$ = 7.48 (s, 2H), 7.04 (s, 2H), 6.66 (s, 4H), 6.57 (s, 2H), 6.55 (s, 2H), 4.03 (m, 8H), 1.39 ppm (m, 12H); $^{13}$C NMR ($C_2D_2Cl_4$, 90 °C): $\delta$ = 153.3, 151.81, 151.77, 140.5, 136.9, 136.4, 133.8, 133.2, 133.0, 129.0, 122.7, 118.7, 118.1, 117.7, 68.3, 68.0, 17.0, 17.8 ppm; elemental analysis calcd (%) for $C_{32}H_{24}N_2O_4$: C 77.68, H 5.79; N, 5.03; found: C77.39, H 5.80; N, 5.27.

**Molecular tweezers 4a**: To a solution of **3a** (250 mg, 0.5 mmol) in $CH_2Cl_2$ (60 mL) was added DIBAL-H (1 M solution, 4 mL, 4.0 mmol) at −78 °C under an $N_2$ atmosphere. After stirring for 2 h, the reaction was quenched by addition of aqueous saturated $NH_4Cl$ solution. The mixture was extracted with $CH_2Cl_2$. The organic layer was washed with water and brine and then dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, $CHCl_3$/EtOAc v/v = 10:1). Recrystallization from DMF gave **4a**. Yield: 100 mg, 0.19 mmol (39.5 %); yellow crystals; m.p. 277–278 °C (decomp); MS (LDI-TOF): *m/z*: 506 $[M]^+$; $^1$H NMR ($CDCl_3$): $\delta$ = 9.74–9.73 (s × 2, 2H), 7.57–7.54 (s × 2, 2H), 6.77–6.76 (s × 2, 2H), 6.74–6.53 (m, 8H), 3.87–3.80 ppm (m, 12H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 193.0, 192.8, 154.0, 153.6, 149.7, 149.5, 148.4, 148.3, 143.7, 143.6, 136.5, 136.4, 132.6, 132.4, 132.4, 131.9, 131.8, 131.8, 131.1, 130.7, 129.7, 129.6, 127.1, 126.8, 112.0, 111.9, 110.9, 110.8, 56.0, 55.9, 55.8, 55.7 ppm; HR-MS (EI): *m/z*: calcd for $C_{32}H_{26}O_6S_2$ $[M]^+$: 506.1729; found: 506.1707.

**Molecular tweezers 4b**: Compound **4b** was prepared by a procedure similar to that used for **4a**. Yield: 360 mg, 0.640 mmol, 81.0 %; yellow crystals from $CH_2Cl_2$/hexane; m.p. 250–252 °C (decomp); MS (LDI-TOF): *m/z*: 562 $[M]^+$; $^1$H NMR ($CDCl_3$): $\delta$ = 9.72–9.71 (s × 2, 2H), 7.55–7.52 (s × 2, 2H), 6.75–6.74 (s × 2, 2H), 6.72–6.51 (m, 8H), 4.09–3.99 (m, 8H), 1.45–1.38 ppm (m, 12H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 193.1, 192.9, 154.2, 153.9, 149.5, 149.3, 148.0, 147.9, 143.6, 143.5, 136.5, 136.4, 132.7, 132.4, 132.2, 131.8, 131.7, 131.7, 131.1, 130.7, 129.8, 129.6, 126.9, 126.8, 113.8, 113.5, 113.0, 112.8, 64.7, 64.5, 64.4, 64.3, 14.8, 14.7 × 2, 14.6 ppm; elemental analysis calcd (%) for $C_{32}H_{24}N_2O_4$: C 76.85, H 6.09; found: C76.81, H 6.12.

**Molecular tweezers 5b**: To a solution of **4b** (107 mg, 0.19 mmol) in THF (50 mL) was added $NaBH_4$ (8 mg, 0.20 mmol) at 0 °C under an $N_2$ atmosphere. After the mixture was stirred for 3 h, the reaction was quenched by addition of aqueous saturated $NH_4Cl$ solution, and the mixture was extracted with $CHCl_3$. The organic layer was washed with $H_2O$ and brine and then dried over magnesium sulfate. After evaporation of the solvent, the residue was dissolved in THF (20 mL) and the solution was added to a suspension of NaH (60 %, in oil; 85 mg, 2 mmol) in THF (20 mL) under an $N_2$ atmosphere. After the mixture was stirred for 10 min, $CH_3I$ (0.6 mL, 9.7 mmol) was added dropwise and stirred overnight at 60 °C. The reaction was quenched by addition of $H_2O$, and the mixture was extracted with $CH_2Cl_2$. The organic layer was washed with $H_2O$ and brine, and then dried over magnesium sulfate. After evaporation of solvent, the residue was purified by column chromatography (silica gel, $CHCl_3$/EtOAc v/v = 10:1). Recrystallization from $CH_2Cl_2$/hexane gave **5b**. Yield: 76.6 mg, 0.13 mmol (68.4 %, 2 steps); colorless powder; m.p. 236.5–237.5 °C (decomp); MS (LDI-TOF) *m/z*: 594 $[M]^+$; $^1$H NMR ($CDCl_3$): $\delta$ = 6.81–6.79 (s × 2, 2H), 6.69–6.67 (s × 2, 2H), 6.67–6.57 (6.65 (d, $J$ = 10.0 Hz), 6.62(s), 6.59 (d, $J$ = 10.0 Hz), 4H), 6.55–6.54 (s × 2, 2H), 6.50–6.47 (s × 2, 2H), 4.26–4.07 (m, 4H), 4.05–3.96 (m, 8H), 3.40–3.38 (s × 2, 6H), 1.42–1.36 ppm (m, 12H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 147.8 × 2, 147.6, 147.4, 139.5, 139.4, 137.2, 137.0, 136.7, 136.6, 133.4, 133.3, 131.7, 131.6, 130.3, 129.8, 129.6, 129.4, 129.4, 129.3, 128.6, 128.0, 113.6, 113.5, 113.4, 113.1, 64.5., 64.4, 64.3, 64.2, 58.1 × 2, 57.9 × 2, 14.8 × 4 ppm; HR-MS (EI): *m/z*: calcd for $C_{38}H_{42}O_6$ $[M]^+$: 594.2941; found: 594.2981.

**X-ray structural analysis**: Intensity data were collected on a Bruker SMART APEX diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), a Rigaku AFC7R diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71069 Å), and Rigaku Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å). The structure was solved by direct methods (SHELXTL) and refined by the full-matrix least-squares method on $F^2$ (SHELXL-97). All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed using AFIX instructions.

**4a**: Single crystals were obtained by recrystallization from DMF. $C_{32}H_{26}N_6{\cdot}2C_3H_7NO$; $FW$ = 652.73, triclinic, $P\bar{1}$, $a$ = 9.402(2), $b$ = 11.334(3), $c$ = 9.2127(11) Å; $\alpha$ = 105.388(14), $\beta$ = 95.383(14), $\gamma$ = 112.766(19)°; $V$ = 851.3(3) Å$^3$, $Z$ = 1; $\rho_{cald}$ = 1.273 g cm$^{-3}$. The refinement converged to $R_1$ = 0.0483, $wR_2$ = 0.1460 [$I > 2\sigma(I)$], $GOF$ = 0.999.

**TCNB@4b**: Single crystals were obtained by recrystallization from $CHCl_3$. $C_{36}H_{34}O_6{\cdot}C_{10}H_2N_4{\cdot}CHCl_3$; $FW$ = 860.16, triclinic, $P\bar{1}$, $a$ = 10.761(3), $b$ = 13.910(4), $c$ = 15.552(4) Å; $\alpha$ = 84.952(5), $\beta$ = 73.093(4), $\gamma$ = 76.461(4)°; $V$ = 2164.8(10) Å$^3$; $Z$ = 2; $\rho_{cald}$ = 1.320 g cm$^{-3}$. The refinement converged to $R_1$ = 0.0680, $wR_2$ = 0.1953 [$I > 2\sigma(I)$], $GOF$ = 1.025.

**TCNB@5b**: Single crystals were obtained by recrystallization from $CHCl_3$. $C_{38}H_{42}O_6{\cdot}C_{10}H_2N_4$; $FW$ = 772.87, triclinic, $P\bar{1}$, $a$ = 11.2476(16), $b$ = 11.5599(16), $c$ = 16.233(2) Å; $\alpha$ = 92.630(8), $\beta$ = 98.272(7), $\gamma$ = 95.209(7)°; $V$ = 2076.3(5) Å$^3$; $Z$ = 2; $\rho_{cald}$ = 1.236 g cm$^{-3}$. The refinement converged to $R_1$ = 0.0842, $wR_2$ = 0.2031 ($I > 2\sigma(I)$), $GOF$ = 1.292.

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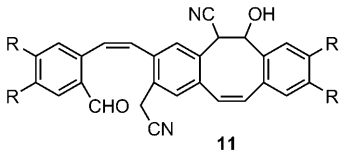


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