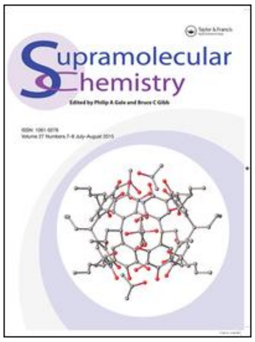

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Synthesis, characterization and selective Cu^{2+} recognition of novel E– and Z–stilbenophanes

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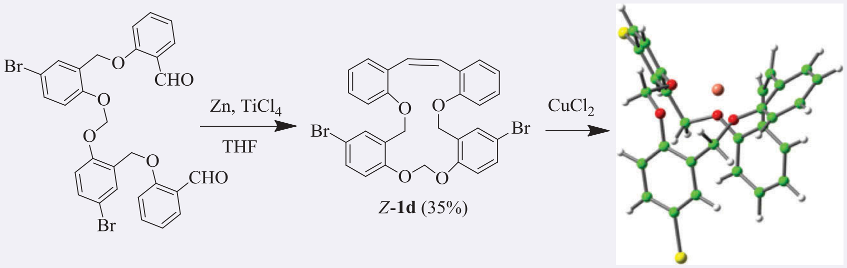
ABSTRACT
We have demonstrated the synthesis and characterization of novel *E*- and *Z*-stilbenophanes *via* four reaction steps. X-ray structure analysis showed that the p-electrons of the double bonds and the oxygen atoms pointing towards the center of a cavity of *Z*-isomer. Both isomers recognize selectively Cu^{2+} ions over other competing metal ions as measured by UV-vis titration by the detection limit 10–12 µM. The 1:1 ratio complex formation was confirmed by HRMS analysis. Theoretical calculations based on GIAO and CMAD approaches and ^{1}H NMR analysis confirmed the UV-vis data of Z-isomer.



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KEYWORDS
Stilbenophane; synthesis; Cu^{2+} ion recognition; theoretical calculations

Introduction

Supramolecular chemistry is a relatively young area of interdisciplinary field of science which is located at the intersection of chemistry, biology, and physics (1–5). The preparation method, characterization and application of receptors are the principles of supramolecular chemistry to make nonbonding supramolecular interactions with substrates.

One of the defining concepts of supramolecular chemistry is host–guest chemistry in which the non-covalent interactions leads to the formation of unique structural complexes. The binding ability of a host is depended to its size, shape, rigidity, receptor sites and the cavity. Therefore, to tune the binding ability of a host, a careful design of the host is needed.

Stilbenophanes are macrocyclic molecules which accomplished by linking the various positions of stilbene moiety with an appropriate bridging moiety. They have attracted attention in various fields from physicochemical and molecular recognition (6–10) to biological activity (11, 12).

In the past few years, we have prepared a series of 2,2′-stilbenophanes **1** and **2** (Scheme 1) which are resulted from a combination of alkyl chain length and the configuration of alkene of stilbene moeity (13–20). The application of these molecules as sensor of metal ions has been successful because of the suitable shape, stereochemistry and cavity size of host. For example, the host **1c** recognizes Li^+ ions (14), while *Z,Z*-**1b** (16) and *E,E*-**1a** (18) host the silver ions. On the other hand, stilbenophanes **1b** and **1c** are suitable hosts for Pd^{2+} ions as evidenced from their self-activation in Wacker oxidation (19, 20).

Herein, we wish to report the synthesis and characterization of new stilbenophanes *E*-**1d** and Z-**1d**. Based on the ability of crown ethers and as well as π-electron systems to host metal ions (21–23), we also studied the host-guest chemistry of **1**. Accordingly, both isomers exhibited selective optical sensing toward Cu^{2+} ions among various metal

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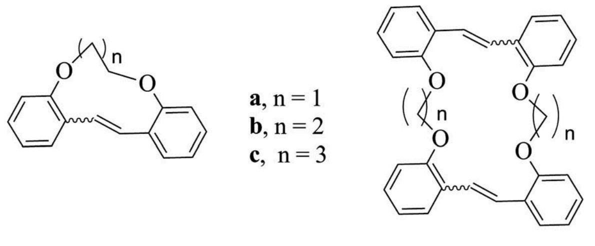
supplemental data for this article can be accessed here.



Scheme 1. A series of prepared stilbenophanes **1** in our lab.

ions. The existence of bromines on the two sides of molecular ring gives this chance to make a polymer (24–26) for the selective adsorption of Cu^{2+} ions.

Results and discussion

The four steps synthesis of *E*-**1d** and Z-**1d** are shown in Scheme 2. The carbonyl groups of dialdehyde **5** were reduced by sodium borohydride to give **4** in 95% yield. The dibenzil **4** was then treated with excess amount of bromine in CH_2Cl_2 to give brominated product of **3** in 95% yield, which in turn, was coupled with 2.3 equiv. of salisaldehyde in the presence of K_2CO_3 in DMF to provide the precursor **2** in 92% yield.

Finally, the intramolecular coupling of the dialdehyde **2** with low-valent titanium, prepared from refluxing $TiCl_4$ and Zn in THF, gave a mixture of *Z*-**1d** and *E*-**1d**. The crude products were purified on silica gel eluted with hexane–ethyl acetate (7:3) to afford, in order of elution, *Z*-**1d** and *E*-**1d** in 35% and 30% yield, respectively.

The structures of the cyclophanes *E*-**1d** and *Z*-**1d** were determined by NMR spectroscopic data. Both isomers are highly soluble in common solvents. Therefore, we measured their ^1H and ^{13}C NMR spectra in $CDCl_3$ and found the asymmetric structure of products (Figures S11-S15).

In both isomers, the alkene protons appear as one sharp singlet. The cis-geometry was assigned to the isomer with lower chemical shift value for the vinylic protons (7.37 ppm for *E*-**1d** and 6.60 ppm for *Z*-**1d**). Moreover, the chemical shifts of aromatic hydrogens of *E*-**1d** are more deshielded and expanded than those of *Z*-**1d** (6.80–7.50 ppm for *E*-**1d** and 6.65–7.45 ppm for *Z*-**1d**). The expected peak of each methylene group was observed as singlet. The number of observed signals agrees with the expected number of carbons in both isomers.

X-ray crystallographic analysis at 298K confirmed the molecular structure of *Z*-**1d** and determined its geometry (27). Two different views of the molecules are shown in Figure 1 and Figure S16. The compound crystallizes in the monoclinic system and $P2_1/c$ space group. The

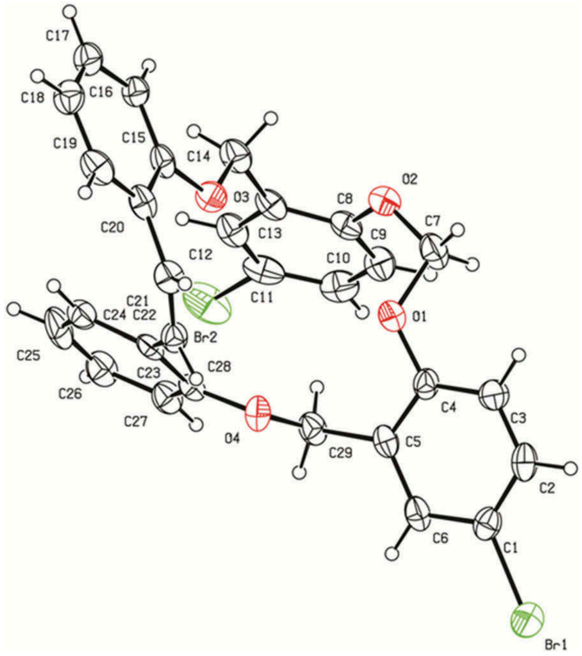
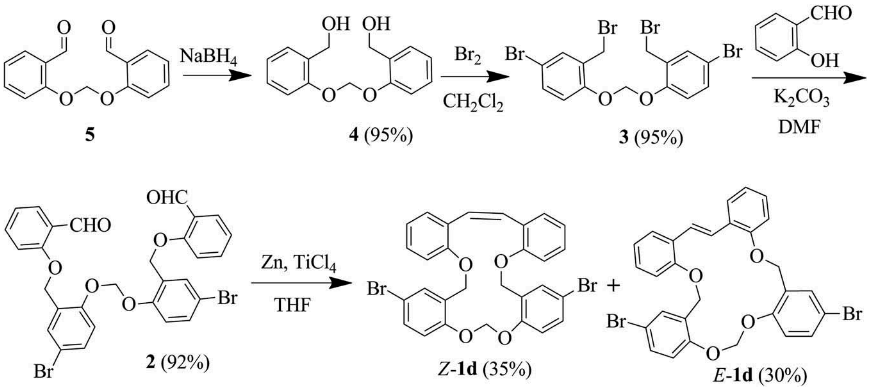


Figure 1. The molecular structure of *Z*-**1d.**



Scheme 2. The synthesis of *E*- and *Z*-stilbenophane **1d.**

ethene bridge [C (21)-C (22)] exhibits a cis configuration, in agreement with the ^{1}H NMR spectrum, with considerably widened bond angles 129.8 (7)° for C (20)-C (21)-C (22). As shown in Figure S16, the molecular structure of *Z*-**1d** contains a rectangular cavity with dimensions that are defined by the distance between the two facing oxygen atoms (~ 4.0 Å). Two facing phenyl units are almost parallel with respect to each other with a torsion angle of about 158 with a weak π–π interaction (4.3 Å). The phenylene rings of stilbene moiety are rotated by about 40-45° with respect to double bond. As a consequence, the π-electrons of both the double bonds and the oxygen atoms point into the cavity to accommodate the guest. In contrast, bromide atoms are out of cavity.

It is noteworthy to mention that the McMurry coupling of the non-brominated dialdehyde **2′** did not give any amounts of stilbenophanes **1′** (Figures S17-19). It means that the bromines play an important role on the intramolecular cyclization of the dialdehyde **2**.

The UV-vis spectra of compounds *E*-**1d** and *Z*-**1d** exhibited two and one main absorbance bands, respectively. To evaluate the binding ability of both isomers toward different transition metal ions, the UV-vis spectrophotometric titration were carried out by the addition of metal ions to ligands **1** in a quartz cell in CH_3CN solutions. Except Cu^{2+}, no noticeable changes were observed with other metals (Li^+, Na^+, Ni^{2+}, Co^{2+}, Cu^+, Pd^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+} and Pb^{2+}) under the same conditions.

The addition of $CuCl_2$ to solution of *E*-**1d** and *Z*-**1d** induced a dramatic change in the UV-vis spectrum which are diagnostic for changes in the electronic structure of the molecules (Figure 2). While absorbance intensity of *Z*-**1d** at 280 was gradually decreased, a new peak around 310 nm was appeared upon gradual addition of Cu^{2+} ions. On the other hand, changes in the UV-vis spectrum of *E*-**1d** was different with those of *Z*-**1d**. upon addition of Cu^{2+} ions, the absorbance intensity at 280 nm was gradually increased, while peak around 330 nm was decreased. It means that conjugation of stilbene moiety of *E*-**1d**, unlike *Z*-**1d**, are decreased during the complex formation. The isosbestic point in the absorption spectra of both isomers was observed to clearly indicate the formation of receptor-cation complex in the solution. From the binding constant calculation of both isomers of **1d** with Cu^{2+} (28), the obtained detection limit of both isomers for Cu^{2+} ions were found to be 10–12 μM which is lower than the maximum allowable level of Cu^{2+}ions (31.5 μM) in drinking water set by the WHO (29).

The optical response arises from the 1:1 complexation of **1d** with the Cu^{2+} ions as evidenced from high resolution mass spectrum (HRMS) data showing a peak at m/z 654.9365 (Figures S10 and S20).

The ^{1}H-NMR spectra were recorded in DMSO-d6 and the assignments of *Z*-**1d** and *Z*-**1d**@Cu^{2+} are shown in Figure 3. It was found that all ^{1}H NMR signals of *Z*-**1d** are shifted slightly downfield (*ca* 0.06–0.09 ppm) upon complexation with $CuCl_2$. Consequently, the results of both UV-vis and ^{1}H-NMR analysis indicates that conjugation between two aryl groups are increased during the complex formation.

To obtain more information about the structure of complex *Z*-**1d**@Cu^{2+}, our attempts to obtain suitable single crystals of complex for X-ray studies failed. On the other hand, the data obtained by NMR and UV-vis analysis need more support to show the certain position of Cu^{2+} ion in resultant complex.

To this end, we resort to some computational results to circumvent this problem by using all probable positions of Cu^{2+} ion in complex (Table S1 and Figure 4). These solution state computational results are obtained from geometry optimization followed by chemical shielding and excited state calculations. Geometry optimization and chemical shielding calculations using density functional theory (DFT) employ ONIOM(B3LYP/6–311 + g(d,p): BP86/TZVP) and B3LYP/6–311 + G(d,p) levels of theory for

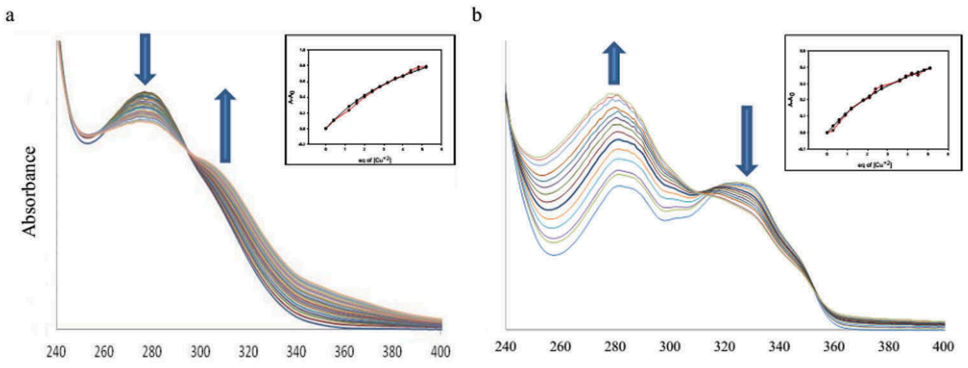


Figure 2. UV–vis spectra of (a) *Z*-**1d** and (b) *E*-**1d** upon addition of Cu^{2+} in CH_3CN.

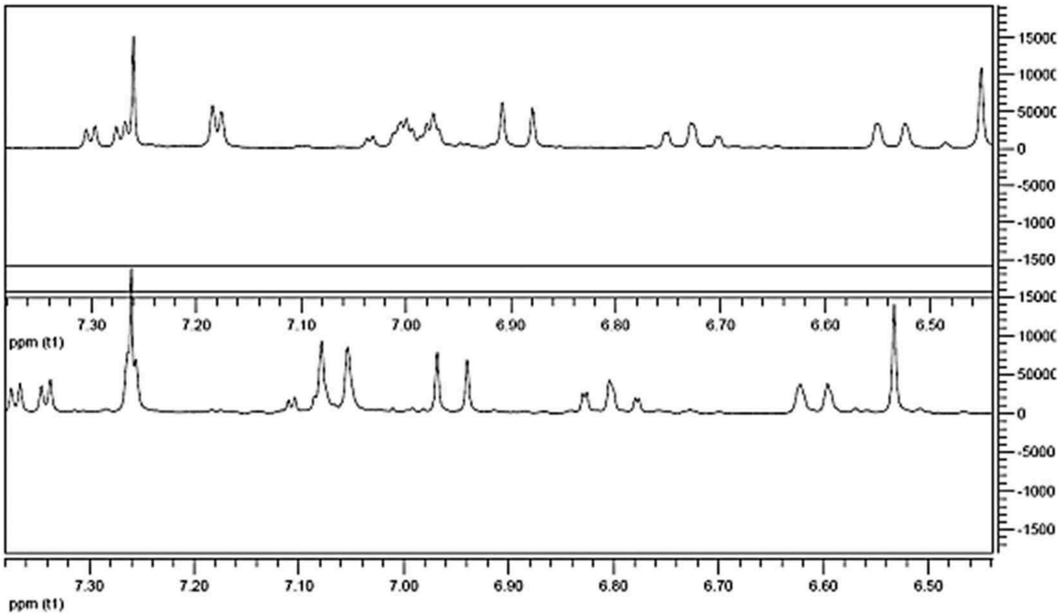


Figure 3. ^{1}H NMR spectroscopy of *Z*-**1d** (above) and *Z*-**1d**@Cu^{2+} (below) in DMSO-d6.

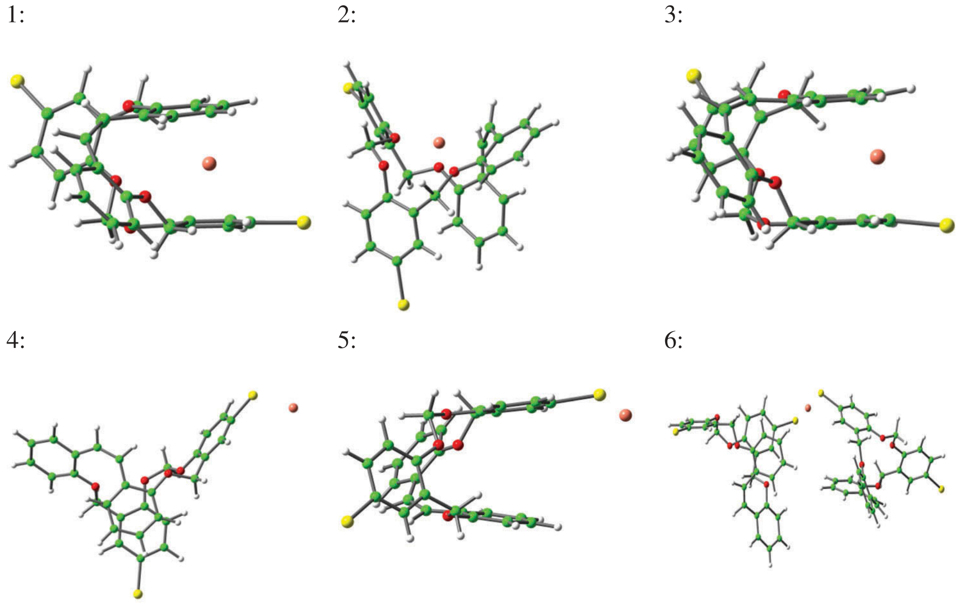


Figure 4. Optimized geometries of *Z*-**1d**@Cu^{2+}. The most probable structures 1–6 are shown.

complex and free ligand states, respectively. The BP86/TZVP and B3LYP/6–311 + G(d,p) levels of theory are used for Cu^{2+} ion and *Z*-**1d** in ONIOM calculations, respectively (Figure 4). Gauge invariant atomic orbital (GIAO) condition is applied in the chemical shielding calculations (30). Time dependent DFT (TD-DFT) calculations of excited states are run at cam-B3LYP/6–31++ G(d,p) level of theory in both complex and free ligand solutions. The conductor-like polarizable continuum model (CPCM) is used for chloroform solvent (31). All calculations are run using ORCA software (32). Calculated and experimental chemical shift values beside calculated relative energies are summarized in Table S1. While relative energies suggest complexes 1 and 2 as most stable and consequently most probable structures, calculated corrected mean absolute deviations (CMAD) of shift values do not provide tight support for this conclusion.

To select one of these two structures as probable structure in observed experiment, we resort to calculated UV-Vis spectra obtained from excited state calculations. Between the structures 1 and 2, the former shows similar peaks in accordance with experimental spectra to suggest the most probable structure of complex under experimental condition. Therefore, the most possible structure of complex is that Cu^{2+} is coordinated with oxygen atoms (structure of 2 in Figure 4).

Conclusion

In conclusion, we have demonstrated the syntheses and spectral properties of novel *E*- and *Z*-stilbenophanes **1d** for the first time. The crystal structure of *Z*-**1d** was also achieved. Both isomers act as colorimetric chemosensors for Cu^{2+} ions over other competing metal ions. To estimate the structure of complex, UV-vis and ^1H NMR analysis together with theoretical calculation of UV-vis analysis were investigated. Therefore, the most possible structure of complex is resulted from the coordination between Cu^{2+} and four oxygen atoms of host.

Experimental

Materials and methods

The experiments were conducted in flame-dried glassware under an inert atmosphere of argon unless otherwise noted. The solvents and reagents used in each experiment were dried and purified according to accepted procedures. Melting points are determined on Büchi 530 and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 and 500. All NMR samples were run in $CDCl_3$ and chemical shifts are expressed as ppm relative to internal Me_4Si. Mass spectra were obtained on a Fisons instrument. Column chromatography was carried out with the use of Merck Art.7734 kieselgel 60, 70–230 mesh ASTM. Tetrahydrofuran (THF) and CH_3CN were freshly distilled under a nitrogen atmosphere from sodium-benzophenone prior to use. The solutions of metal ions were performed from their chloride salts and the stock solution was prepared in CH_3CN.

General procedure for the preparation of compounds 4

Sodium borohydride (26.5 mg, 0.7 mmol) was gradually added to a solution of **5** (0.256 g, 1 mmol) in 1:1 ratio of THF and C_2H_5OH (25 ml) while it stirred in the ice-water bath. After the addition was ended, the reaction mixture was stirred for 2h. After completion of the reaction as indicated by TLC, H_2O (30 ml) was added and a white precipitate formed. The product was extracted by EtOAc (30 ml) and gave a pure white powder of **4** in 95% yield.

Compound **4**: White solid, m.p. = 121-123°C; ^1H NMR (500 MHz, DMSO-d_6) 7.41 (dd, 2H, PhH), 7.25 (t, 2H, PhH), 7.20 (dd, 2H, PhH), 7.04 (t, 2H, PhH), 5.87 (s, 2H, O- CH_2-O), 5.03 (t, 2H, -OH), 4.46 (d, 4H, CH_2OH).; ^{13}C NMR (125 MHz, DMSO) δ 153.6, 132.0, 128.1, 127.8, 122.4, 114.3, 90.9, 58.2.; IR (KBr, cm^{-1}): 3298, 2925, 2864, 1597, 1490, 1457, 1215, 1112, 1043, 1013, 750, 431.

Procedure for the preparation of compounds 3

An excess amount of Br_2 (1.2 g, 7.72 mmol) was added to a solution diol **4** (0.5 g, 1.93 mmol) in CH_2Cl_2 (25 ml) at room temperature. The dark red solution of reaction mixture was stirred for 12 h. The progress of reaction was monitored by TLC. The remained Br_2 was quenched with saturated sodium thiosulfate in H_2O. The organic compounds were extracted with CH_2Cl_2 (3 × 10 ml) and were dried over anhydrous $NaSO_4$. After removing solvent, a yellow solid was obtained which was crystallized by boiling hexane to give a pure white solid of **3** in 95% yield.

Compound **3**: White solid, m.p. = 177 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.5 Hz, 2H), 7.45 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 5.88 (s, 2H), 4.47 (s, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$): 153.7, 133.7, 133.0, 129.2, 116.6, 115.1, 91.1, 27.1.; IR (KBr, cm^{-1}): 2973, 1484, 1310, 1223, 1185, 1144, 1019, 871, 807,612, 519.

Procedure for the preparation of compounds 2

Salisaldehyde (0.21 g, 1.8 mmol) and K_2CO_3 (0.34 g, 2.5 mmol) was added to DMF (15 ml) at room temperature and stirred for 1 hour. Then **3** (0.485g, 0.9 mmol) was added to the mixture and stirred for 3 hours. Then water (40 ml) was added to the solution and a white precipitate formed. After it was filtered and a white solid obtained.

Compound **2**: White solid, ^1H NMR (300 MHz, CDCl3): 10.48 (s, 2H), 7.86 (dd, 2H), 7.61 (d, J = 1.8 Hz, 2H), 7.50 (t, J = 7.2 Hz, 2H), 7.42 (dd, J = 8.7 Hz, J = 2.1 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 7.5 Hz, 2H), 6.88 (d, J = 7.5 Hz, 2H), 5.84 (s, 2H), 5.08 (s, 4H).; ^{13}C-NMR (75 MHz, CDCl3): 189.3, 160.6, 152.9, 135.9, 132.3, 131.9, 128.7, 128.1, 125.2, 121.3, 116.0, 115.7, 112.8, 91.2, 65.1.; IR (KBr, cm-1): 1600, 1482, 1394, 1283, 1218, 1138, 1100, 993, 831, 758.

Procedure for the preparation of compounds 1d

To a stirred suspension of Zinc powder (0.07 g, 1.1 mmol) in 15 ml dry THF, $TiCl_4$ (0.062 ml, 0.55 mmol) was injected slowly at 0 ºC under an argon atmosphere. The obtained black suspension was gradually warmed to room temperature and then refluxed for 2 h. A solution of dialdehyde **2** (0.15 g, 0.23 mmol) in THF (15 ml) was added dropwise to the above reaction mixture at room temperature, and the resulting mixture was refluxed for an additional 6 h. The reaction mixture was cooled to room temperature and quenched with 10% aqueous K_2CO_3 (30ml). The organic layer was separated and the aqueous suspension was extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, evaporated and chromatographed on silica gel using a mixture of ethyl acetate and hexane to afford compound *E*-**1d** (30% yield, rf = 0.62 at 1:8 mixture of ethyl acetate and hexane) and *Z*-**1d** (35% yield, rf = 0.55).

Compound *Z*-**1d**. Colorless solid, mp = 168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, $CDCl_3$): 7.42 (dd, *J* = 8.6, 2.5 Hz, 2H), 7.33 (d, *J* = 2.5 Hz, 2H), 7.16 (dd, *J* = 7.5, 1.5 Hz, 4H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.99 (t, *J* = 8.7, 2H), 6.67 (dd, *J* = 8.7, 1.2 Hz, 2H), 6.60 (s, 2H), 5.59 (s, 2H), 4.66 (s, 4H); ^{1}H NMR (300 MHz, DMSO-d_6: $CDCl_3$ [1:9]): 7.34 (dd, *J* = 8.6, 2.5 Hz, 2H), 7.26–7.27 (m,2H), 7.05–7.10 (m, 4H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.80–6.83 (m, 2H), 6.62–6.60 (m, 2H), 6.53 (s, 2H), 5.53 (s, 2H), 4.60 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): 155.6, 154.3, 133.4, 132.2, 131.1, 130.6, 128.4, 128.2, 127.1, 121.2, 119.5, 116.4, 114.3, 95.5, 65.4; HRMS, m/z (rel. Intensity %) Calculated: 593.99 (M+); found: 593.0143 (M+ nH), 614.9966 (M+ nNa).

Compound *E*-**1d**. Colorless solid, mp = 170 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 2.5 Hz, 2H), 7.37 (dd, *J* = 8.7, 2.4 Hz, 4H), 7.27 – 7.20 (m, 2H), 7.07 (s, 2H), 7.04 – 6.95(m, 6H), 5.73 (s, 2H), 4.97 (s, 4H). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.69 (d, J = 2.5 Hz, 2H), 7.63 – 7.40 (m, 4H), 7.28 (s, 2H), 7.22 (dd, J = 3.8, 1.0 Hz, 4H), 7.14 (d, J = 8.8 Hz, 2H), 6.92 (m, 2H), 5.97 (s, 2H), 5.01 (s, 4H).^{13}C-NMR (75 MHz, DMSO-d_6): 156.7, 155.4, 134.3, 133.0, 129.23, 129.23, 129.1, 128.3, 128, 128, 121.7, 117.5, 115.2, 114, 93.1, 67.3.; HRMS, m/z (rel. Intensity %) Calculated: 593.99 (M$^+$); found: 593.0143 (M + nH), 614.9966 (M + nNa).

Acknowledgments

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Disclosure statement

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(27) X-ray data for **Z1d**: $C_{29}H_{22}Br_2O_4$, M = 594.27, monoclinic system, space group $P2_1/c$, a = 13.179(3) A, b = 8.5689(17), c = 21.900(4) Å; β = 98.70(3)° V = 2444.7(9) Å^3, Z = 4, D_{calcd} = 1.615 g cm^{-3}, μ(Mo-Kα)= 3.350 mm^{-1}, crystal dimension of 0.50 × 0.50×0.40 mm. The X-ray diffraction measurement was made on a STOE IPDS 2T diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by using SHELXS. The Data reduction and structure refinement was carried out with SHELXL using the X-STEP32 crystallographic software package [*X-STEP32 Version 1.07b, Crystallographic Package*; Stoe & Cie GmbH: Darmstadt, Germany, 2000]. The non-hydrogen atoms were refined anisotropically by full matrix least-squares on F^2 values to final R_1 = 0.0640, wR_2 = 0.1633 and S = 0.805 with 316 parameters using 4292 independent reflection (θ range = 2.26-25°). Hydrogen atoms were added in idealized positions. The crystallographic information file has been deposited with the Cambridge Data Centre, CCDC 1556553.

(28) Since the detection limit using the S/B ratio is regarded as the most reliable and accurate, the detection limit for Cu^{2+} ions using the S/B ratio was determined on the basis of a plot of the ratio of the intensity versus the concentration of Cu^{2+}.

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