New Crown Compounds Containing a 1,3,4-Thiadiazole Moiety: Synthesis and Crystal Structure

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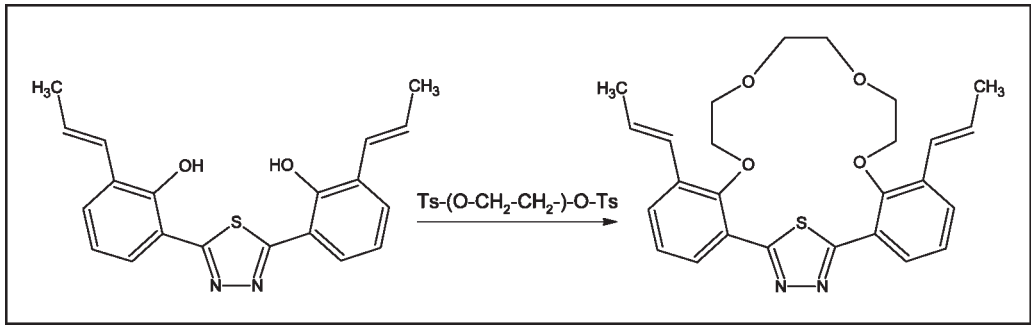

The syntheses of new macrocyclic compounds are described. The 2,5-bis(hydroxyphenyl)-1,3,4-thiadiazole reacts with allyl bromide to give the corresponding allyloxy derivative. The allyl is used to functionalize the ortho position by means of a Claisen rearrangement under microwave irradiation. New 2,5-dihydroxyphenyl-1,3,4-thiadiazoles are obtained, which are converted into macrocyclic polyethers. The structures of the new macrocyclic compounds were confirmed by ^{1}H, ^{13}C NMR, and mass spectroscopy. The crystal structure of 2,5-bis(2-allyloxyphenyl)-1,3,4-thiadiazole has been determined.

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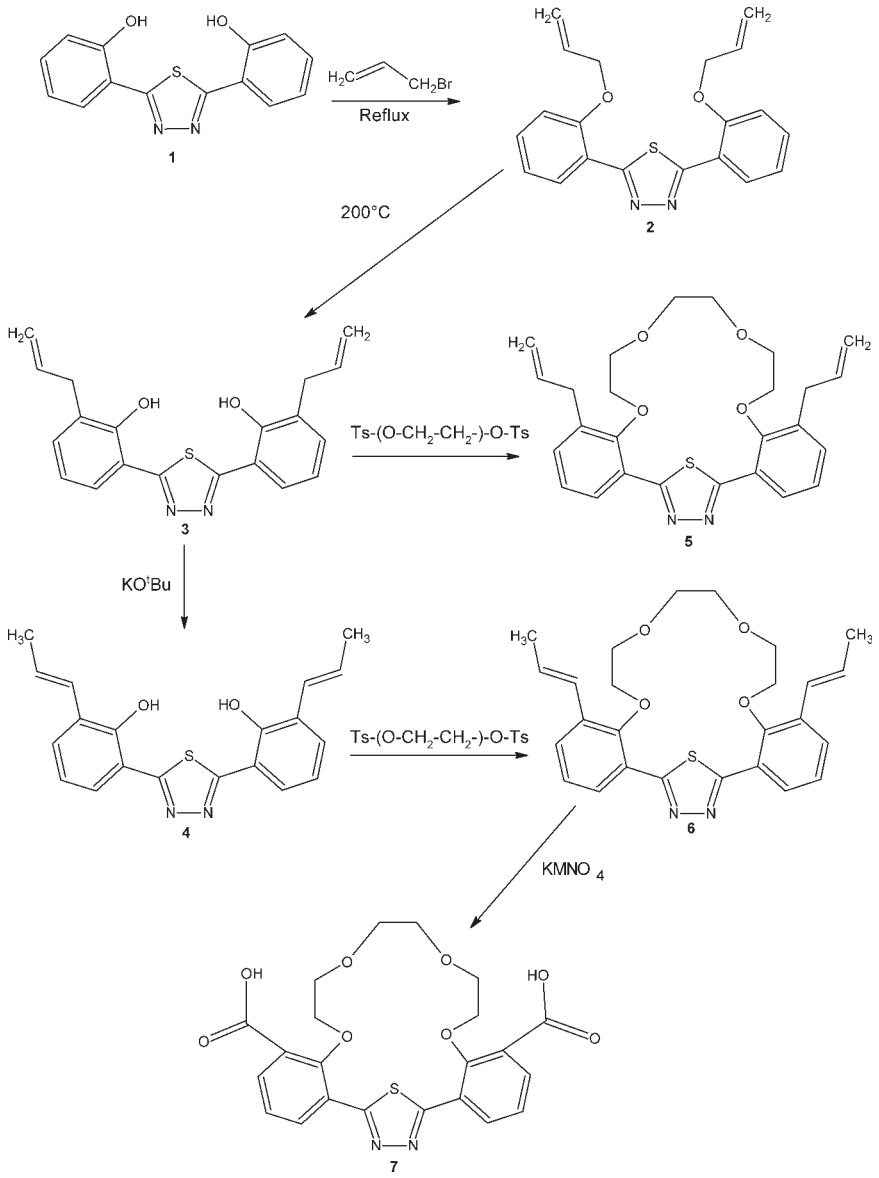
INTRODUCTION

In the field of supramolecular chemistry, crown ethers (CEs) belong to the most popular hosts, because their inclusion complexes have found a vast number of practical applications [1]. Growing interest has focused on the construction of synthetic macrocyclic polyether compounds containing heterocyclic subunits because these compounds have been shown to possess great ability to undergo selective complexation with charged as well as neutral species [2–4]. Cation complexing properties of synthetic macrocyclic polyether ligands containing a heterocyclic subcyclic unit, such as pyridine, have been previously studied by Bradshaw *et al*. using calorimetric technique for the reaction of Na^+, K^+, Ag^+, NH_4^+, and Ba^{2+} [5]. Series of such compounds containing diaryl-1,3,4-oxadiazoles and thiadiazoles have been reported recently [6–8]. In light of the general interest on the construction of synthetic macrocycles containing heterocyclic subunits as well as limited example of 1,3,4-thiadiazole inclusion in a macrocyclic framework, we report in this article the synthesis of new macrocyclic polyethers containing 2,5-diaryl-1,3,4-thiadiazole. These new macrocyclic compounds are expected to show coordinating behaviors toward cations, water, and organic molecules, such as amines or urea. Similar compounds such as crown-annelated oligothiophenes have been previously used as model compounds for molecular actuation [9]. In this work, the cation complexing properties were analyzed by ^{1}H NMR titration experiments with solution of Ba^{2+}, Sr^{2+}, or Pb^{2+}. More recently, the metal cation complexing properties of crown-annelated oligothiophenes containing 3,4-ethylenedioxythiophene have been studied showing that one of these compounds exhibit interesting complexing properties for Pb^{2+} [10]. The problem of recognition and selective binding of ions occupies a prominent place in separation process, especially in radiochemical technologies. For example, the extraction of uranium and of transuranium and rare-earth metals from nitric acid solutions with various functionally substituted CEs has been investigated by Yakshin *et al*. [11]. Recently, some macrocyclic polyether compounds containing a 1,3,4-thiadiazole moiety have been used as corrosion inhibitors for mild steel in acidic media [12]. The existing data show that most organic inhibitors act by adsorption on the metal surface [13], and it was discovered that the corrosion inhibition may be enhanced

Scheme 1



by various chemicals additives such as cation salts. Macrocyclic derivatives with potential complexing properties are expected to be useful for this purpose.

RESULTS AND DISCUSSION

The 2,5-bis (2-hydroxyphenyl)-1,3,4-thiadiazole **1** reacts with allyl bromide in the presence of solid potassium carbonate suspended in acetone. The mixture is heated under reflux during 12 h. The end of the reaction is controlled by TLC (thin layer chromatography) using a 50/50 mixture of ethylacetate and petroleum ether as eluent. Under these experimental conditions, the reaction takes place in basic media to allow the deprotonation of the two OH groups, which implies the rotation of the two oxygen atoms to the sulfur side as previously calculated [8]. After evaporation of the solvent *in vacuo*, the solid residue is treated with a solution of sodium hydroxide. The 2,5-bis-(2-allyloxyphenyl)-1,3,4-thiadiazole **2** was collected by filtration, washed with water, and recrystallized from ethanol. The structure proposed for this new thiadiazole derivative is consistent with the data obtained from their ^{1}H, ^{13}C, MS, and elemental analysis.

Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of ethanol, and the crystal structure of compound **2** was investigated (Scheme 1).

The main features of the crystal structure of **2** are resulting from the quasi planarity of the whole entity:

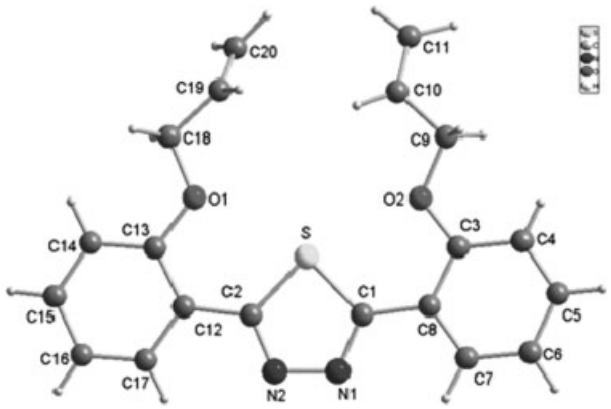


Figure 1. Projection view of compound **2**.

only O2, C10, C11, C18, and C20 are out of the mean plane containing most of the molecule; when using the central thiadiazole ring as planar reference, the phenyl ring on the right (C3 to C8, Fig. 1) is tilted 2° anticlockwise, whereas the other phenyl ring (C12 to C17) is tilted clockwise of 4°. The structure is described by stacking two different layers of such **2** entities along the [001] direction: a first set, located in the (001) basal plane of the unit cell, is seen with molecules of **2** with their central thiadiazole ring pointing upward and downward alternatively, stacked parallel to the [101] direction; a second set with a similar alternating organization of planar entities parallel to the [10-1] axis is seen at about *c*/2. This new ligand with sulfur and two π bonds is offering soft ligation sites and the two oxygen atoms provide hard ligation sites, all five of which are pointed toward a single space and are likely to discriminate between potential metals.

The allyl group was used to functionalize the ortho position to the phenol by means of a Claisen rearrangement. The compound **2** was exposed to microwave irradiation in ethylene glycol at an elevated temperature (200°C). This reaction was conducted under microwave heating to improve the yield and the purity of the product. The double bond of the allyl substituent was isomerized into conjugation with the aryl under basic conditions using potassium *tert*-butoxide [14].

Table 1

Summary of the crystal data and structure refinement for compound **2**.

Formula	C20 H18 N2 O2 S
Formula weight	350.42 g/mol
Crystal system	Monoclinic
Space group	P 21/*n*
a (Å)	*a* = 7.6640(2)
b (Å)	*b* = 16.0490(5)
c (Å)	*c* = 14.2818(4)
α (°)	
β (°)	β = 95.8
γ (°)	
V (Å^3)	1747.6(4)
Z	4
D_{cal} (mg/m^3)	1.33
T (K)	296
F(000)	736
Crystal size, mm	0.1 × 0.1 × 0.1
μ (mm^{-1})	0.201
Data collection range	
Range of indices	*k*, −12 to 12; *h*, −26 to 26; *l*, −23 to 23
Reflections measured	8482
R_{int}	3.91
(R_{all}; $R_{2\sigma}$)	5.99; 4.24
(wR_{all}; $wR_{2\sigma}$)	11.93; 10.77
Goodness of fit	1.02
Number of parameters	298
Maximum peak in final Δ*F* map (e/Å^3)	0.44
Minimum peak in final Δ*F* map (e/Å^3)	−0.28

EXPERIMENTAL

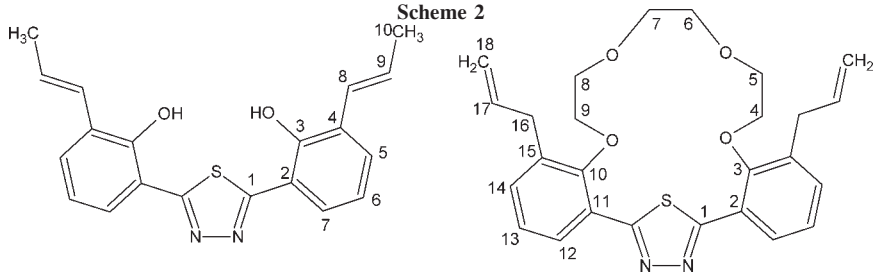
Melting points were determined on an IA 9000 series electrothermal apparatus and are uncorrected. Elemental analyses of C, H, N, and S were performed at the Elemental Analysis service of CNRS, Vernaison, France. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker F.T. AC 300 spectrometer (300

Table 2

Bond distances (Å) and angles (°) for compound **2**.

Bond distances (Å)			
S1—C1	1.727(1)	C9—C10	1.484(2)
S1—C2	1.724(1)	C9—O2	1.432(1)
C1—N1	1.316(1)	C10—C11	1.306(2)
C1—C8	1.470(1)	C12—C17	1.402(1)
N1—N2	1.363(1)	C12—C13	1.407(1)
C2—N2	1.314(1)	C13—O1	1.363(1)
C2—C12	1.471(1)	C13—C14	1.398(1)
C3—O2	1.360(1)	C14—C15	1.381(2)
C3—C4	1.398(1)	C15—C16	1.386(2)
C4—C5	1.385(2)	C17—C16	1.388(2)
C5—C6	1.388(2)	C18—O1	1.441(1)
C7—C6	1.385(2)	C19—C20	1.317(2)
C8—C3	1.402(1)	C19—C18	1.487(2)
C8—C7	1.402(1)		
Angles (°)			
C2—S1—C1	87.82(4)	C3—C8—C1	122.9(1)
C1—N1—N2	113.0(1)	C7—C8—C1	118.9(1)
C2—N2—N1	113.2(1)	O2—C9—C10	108.1(1)
N1—C1—C8	120.2(1)	C17—C12—C13	118.4(1)
N1—C1—S1	113.0(1)	C17—C12—C2	118.7(1)
C8—C1—S1	126.8(1)	C13—C12—C2	122.9(1)
N2—C2—C12	120.3(1)	O1—C13—C14	123.7(1)
N2—C2—S1	113.0(1)	O1—C13—C12	115.9(1)
C12—C2—S1	126.6(1)	C14—C13—C12	120.3(1)
O2—C3—C4	123.7(1)	C15—C14—C13	119.8(1)
O2—C3—C8	115.7(1)	C14—C15—C16	120.9(1)
C4—C3—C8	120.5(1)	C15—C16—C17	119.6(1)
C3—C4—C5	119.7(1)	C16—C17—C12	121.0(1)
C4—C5—C6	120.8(1)	O1—C18—C19	108.0(1)
C6—C7—C8	121.4(1)	C20—C19—C18	123.5(1)
C3—C8—C7	118.2(1)		

Scheme 2



MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) using chloroform ($CDCl_3$) solvent. Matrix-assisted laser desorption ionization (MALDI) and time-of-flight mass spectrometry (TOF-MS) are used to record the mass spectra of the correspondent compounds. All starting materials were of reagent grade and used as purchased.

A single crystal of compound **2** was mounted on a Brucker AXS SMART three-circle diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å), equipped with a CCD two-dimensional detector [15]. Data (Table 1) were corrected for Lorentz, polarization, background, and decomposition effects. Atomic positions were determined using SHELXS [16] and refined using full-matrix least-squares [17]. Hydrogen positions were calculated and included in the final cycles of refinement in constrained positions and with fixed isotropic thermal parameters. Absorption corrections were not made because of the small value of the absorption coefficients (Table 1). Extinction was refined for all three structures but was minimal. Table 2 presents the bond angles and distances for compound **2**. The atomic coordinates and the equivalent displacement are given in Table 3. The anisotropic displacement parameters for compound **2** are presented in Table 4.

General procedure for the synthesis of compounds 1–7. The formula of the parent compounds with corresponding numbers to carbons scheme is given later (Scheme 2).

Synthesis of 2,5-Bis(2-hydroxyphenyl)-1,3,4-thiadiazole (1). Experimental method is reported in the literature [18].

Synthesis of 2,5-Bis(2-allyloxyphenyl)-1,3,4-thiadiazole (2). A mixture of 2,5-bis(2-hydroxyphenyl)-1,3,4-thiadiazole **1** (0.02 mol), anhydrous potassium carbonate (10 g), and allyl bromide (0.04 mol) in acetonitrile (100 mL) was heated under reflux for 12 h with vigorous stirring. The solvent was evaporated *in vacuo,* and the solid residue was heated under reflux with 200 mL of a molar potassium hydroxide solution for 1 h. After cooling, the crude product was filtered, washed with water, and recrystallized from ethanol. Pale yellow solids were obtained: mp 130°C; yield 89%; ^{1}H NMR ($CDCl_3$) δ (ppm) 8.39 (d, J = 8.9 Hz, 2H); 7.54 (t, J = 8.9 Hz, 2H), 7.30 (d, J = 7.5 Hz, 2H); 7.17 (t, J = 7.5 Hz, 2H), 6.20 (m, 2H); 5.53 (d, J_{trans} = 18 Hz, 2H), 5.36 (d, J_{cis} = 9.5 Hz, 2H); 4.84 (d, J = 6.1 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ (ppm) C1 162.68; C2 119.17; C3 155.05; C4 119.30; C5 132.63; C6 121.80; C7 128.21; C8 70.21; C9 133.42; C10 113.89. MALDI-TOFMS: m/z 351 (M + 1). Anal. Calcd. for $C_{20}H_{18}N_2O_2S$: C, 68.55; H, 5.18; N, 7.99; S, 9.15. Found: C, 68.20; H, 5.20; N, 8.06; S, 9.09.

Synthesis of 2,5-Bis[3-allyl-2-hydroxy)phenyl]-1,3,4-thiadiazole (3). 2,5-Bis(2-allyloxyphenyl)-1,3,4-thiadiazole **2** (0.01 mol) was placed in multimode microwave and irradiated for 1 h (300 W) at 200°C in ethylene glycol (40 mL). Water (100 mL) was added to dilute the solvent. The reaction mixture was filtered. The resulting residue was recrystallized from ethanol: mp 150–152°C; yield 82%; ^{1}H NMR ($CDCl_3$) δ (ppm) 11.40 (s, 2H, OH); 7.41 (d, J = 7.8 Hz, 2H), 7.29 (d,

Table 3

Atomic coordinates and equivalent displacement for compound **2**.

Atom	*x/a*	*y/b*	*z/c*	*U* (Å^2)
S1	0.35157(3)	0.07961(1)	0.54044(1)	0.01935(5)
N1	0.3082(1)	0.1719(1)	0.3948(1)	0.0298(2)
N2	0.2275(1)	0.0984(1)	0.3696(1)	0.0298(2)
C1	0.3798(1)	0.1723(1)	0.4825(1)	0.0217(1)
C2	0.2383(1)	0.0433(1)	0.4381(1)	0.0221(1)
C3	0.5449(1)	0.2526(1)	0.6152(1)	0.0237(2)
C4	0.6399(1)	0.3231(1)	0.6472(1)	0.0307(2)
C5	0.6617(1)	0.3882(1)	0.5857(1)	0.0371(2)
C6	0.5910(2)	0.3840(1)	0.4924(1)	0.0393(2)
C7	0.4993(1)	0.3135(1)	0.4607(1)	0.0317(2)
C8	0.4750(1)	0.2464(1)	0.5209(1)	0.0230(1)
C9	0.5977(1)	0.1867(1)	0.7651(1)	0.0303(2)
C10	0.5423(2)	0.1106(1)	0.8132(1)	0.0472(3)
C11	0.5414(2)	0.1046(1)	0.9043(1)	0.0486(3)
C12	0.1556(1)	−0.0390(1)	0.4234(1)	0.0248(2)
C13	0.1644(1)	−0.1009(1)	0.4935(1)	0.0266(2)
C14	0.0828(1)	−0.1779(1)	0.4755(1)	0.0353(2)
C15	−0.0078(1)	−0.1931(1)	0.3886(1)	0.0405(3)
C16	−0.0198(1)	−0.1328(1)	0.3188(1)	0.0412(3)
C17	0.0620(1)	−0.0564(1)	0.3362(1)	0.0331(2)
C18	0.2491(1)	−0.1369(1)	0.6552(1)	0.0327(2)
C19	0.3599(1)	−0.1018(1)	0.7373(1)	0.0357(2)
C20	0.3049(2)	−0.0918(1)	0.8210(1)	0.0453(3)
O1	0.2557(1)	−0.08041(4)	0.5773(1)	0.0284(1)
O2	0.5126(1)	0.18688(4)	0.6711(0)	0.0275(1)
H1	0.453(2)	0.308(1)	0.395(1)	0.040(4)
H2	0.601(2)	0.429(1)	0.451(1)	0.051(5)
H3	0.728(2)	0.437(1)	0.608(1)	0.046(4)
H4	0.686(2)	0.326(1)	0.708(1)	0.036(4)
H5	0.724(2)	0.187(1)	0.761(1)	0.049(4)
H6	0.562(2)	0.237(1)	0.797(1)	0.041(4)
H7	0.519(3)	0.065(1)	0.771(2)	0.090(7)
H8	0.568(3)	0.1556(1)	0.944(1)	0.079(6)
H9	0.502(3)	0.055(1)	0.929(1)	0.072(6)
H10	0.052(2)	−0.014(1)	0.291(1)	0.038(4)
H11	−0.085(2)	−0.142(1)	0.261(1)	0.050(4)
H12	−0.065(2)	−0.246(1)	0.379(1)	0.050(4)
H13	0.097(2)	−0.222(1)	0.523(1)	0.051(4)
H14	0.293(2)	−0.193(1)	0.635(1)	0.041(4)
H15	0.125(2)	−0.142(1)	0.667(1)	0.040(4)
H16	0.480(2)	−0.091(1)	0.728(1)	0.047(4)
H17	0.383(3)	−0.072(1)	0.875(1)	0.068(6)
H18	0.184(2)	−0.104(1)	0.833(1)	0.047(4)

Table 4

Anisotropic displacement parameters for compound **2**.

	U11	U22	U33	U12	U13	U23
S1	0.0197(1)	0.0198(1)	0.0184(1)	0.0020(1)	0.0016(1)	0.0013(1)
N1	0.0307(4)	0.0340(4)	0.0237(3)	−0.0045(3)	−0.0028(3)	0.0078(3)
N2	0.0299(4)	0.0368(4)	0.0219(3)	−0.0052(3)	−0.0018(3)	0.0034(3)
C1	0.0202(3)	0.0239(4)	0.0209(3)	0.0018(3)	0.0021(3)	0.0044(3)
C2	0.0184(3)	0.0274(4)	0.0209(3)	0.0009(3)	0.0029(3)	−0.0016(3)
C3	0.0219(3)	0.0228(4)	0.0269(4)	0.0007(3)	0.0053(3)	−0.0016(3)
C4	0.0285(4)	0.0278(4)	0.0367(5)	−0.0042(3)	0.0080(4)	−0.0081(4)
C5	0.0351(5)	0.0262(5)	0.0514(7)	−0.0074(4)	0.0117(5)	−0.0050(4)
C6	0.0395(5)	0.0268(5)	0.0525(7)	−0.0048(4)	0.0095(5)	0.0090(5)
C7	0.0310(4)	0.0278(5)	0.0366(5)	−0.0011(4)	0.0039(4)	0.0096(4)
C8	0.0212(3)	0.0213(4)	0.0267(4)	0.0015(3)	0.0037(3)	0.0030(3)
C9	0.0308(4)	0.0388(5)	0.0209(4)	−0.0037(4)	0.0014(3)	−0.0036(4)
C10	0.0710(9)	0.0432(7)	0.0249(5)	−0.0145(6)	−0.0069(5)	0.0030(5)
C11	0.0705(9)	0.0474(7)	0.0277(5)	0.0009(7)	0.0047(5)	0.0061(5)
C12	0.0190(3)	0.0282(4)	0.0279(4)	0.0005(3)	0.0055(3)	−0.0078(3)
C13	0.0185(3)	0.0231(4)	0.0388(5)	0.0017(3)	0.0055(3)	−0.0049(4)
C14	0.0238(4)	0.0246(4)	0.0587(7)	−0.0008(3)	0.0090(4)	−0.0083(4)
C15	0.0276(4)	0.0353(6)	0.0604(8)	−0.0052(4)	0.0138(5)	−0.0237(5)
C16	0.0303(5)	0.0528(7)	0.0419(6)	−0.0086(5)	0.0105(4)	−0.0272(5)
C17	0.0271(4)	0.0447(6)	0.0284(4)	−0.0033(4)	0.0069(3)	−0.0135(4)
C18	0.0281(4)	0.0253(4)	0.0450(6)	0.0003(3)	0.0058(4)	0.0119(4)
C19	0.0274(4)	0.0366(5)	0.0426(6)	−0.0006(4)	0.0014(4)	0.0177(5)
C20	0.0462(6)	0.0464(7)	0.0432(7)	−0.0087(5)	0.0047(5)	0.0154(5)
O1	0.0249(3)	0.0239(3)	0.0358(4)	−0.0026(2)	−0.0003(3)	0.0062(3)
O2	0.0329(3)	0.0274(3)	0.0215(3)	−0.0054(3)	−0.0016(2)	−0.0001(2)

J = 7.8 Hz, 2H); 6.94 (t, J = 7.8 Hz, 2H), 6.07 (m, 2H); 5.17 (d, J_{trans} = 17 Hz, 2H), 5.12 (d, J_{cis} = 9.8 Hz, 2H); 3.54 (d, J = 6.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ (ppm) C1 165.90; C2 120.92; C3 153.52; C4 127.20; C5 133.28; C6 116.60; C7 128.84; C8 34.05; C9 136.72; C10 116.60. MALDI-TOFMS: *m/z* 351 (M + 1). Anal. Calcd. for $C_{20}H_{18}N_2O_2S$: C, 68.55; H, 5.18; N, 7.99; S, 9.15. Found: C, 68.33; H, 5.14; N, 8.02; S, 9.14.

Synthesis of 2,5-Bis[2-hydroxy-3-trans-1-propenyl)phenyl]-1,3,4-thiadiazole (4). A suspension of potassium *tert*-butoxide (8.40 g, 75 mmol) in acetonitrile (40 mL) was heated at 120°C under stirring until it was completely dissolved. 2,5-Bis[3-allyl-2-hydroxy)phenyl]-1,3,4-thiadiazole **3** (7.5 mmol) was added and stirring was continued for 10 min. The solvent was evaporated. The residue was treated and recrystallized from ethanol: mp 172°C; yield 61%; ^{1}H NMR ($CDCl_3$) δ (ppm) 11.36 (s, 2H, OH); 7.87 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 7.6 Hz, 2H); 6.95 (t, J = 7.6 Hz, 2H), 6.82 (d, J = 16 Hz, 2H), 6.35 (m, 2H); 1.81 (d, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm) C1 169.98; C2 118.42; C3 157.35; C4 130.27; C5 135.53; C6 121.20; C7 133.92; C8 132.15; C9 125.79; C10 18.95. MALDI-TOFMS: *m/z* 351 (M + 1). Anal. Calcd. for $C_{20}H_{18}N_2O_2S$: C, 68.55; H, 5.18; N, 7.99; S, 9.15. Found: C, 68.30; H, 5.27; N, 7.83; S, 9.11.

General procedure for the synthesis of macrocycles (5) and (6). A mixture of 2,5-bis[3-allyl-2-hydroxy)phenyl]-1,3,4-thiadiazole **3** or 3,5-bis[2-hydroxy-3-trans-1-propenyl)phenyl]-1,3,4-thiadiazole **4** (5 mmol), anhydrous potassium carbonate (24 mmol), and ethylene or polyethylene glycol ditosylate (5 mmol) in 150 mL of nonprotic polar solvent (acetone, acetonitrile, *etc*.) was irradiated in multimode microwave for 9 h. The solvent was evaporated *in vacuo* and the solid residue was heated under reflux with 200 mL of a potassium hydroxide solution for 1 h. After cooling, the crude product was filtered, washed with water, and recrystallized from ethanol.

Macrocycle 5. mp 85°C; yield 31%; 8.28 (d, J = 7.8 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 6.04 (m, 2H), 5.14 (t, J = 17 Hz, 4H); 4.02 (m, 4H), 3.88 (m, 4H), 3.52 (s, 4H); 3.33 (d, J = 6.0 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm) C1 163.72; C2 116.24; C3 154.43; C4 73.98; C5 69.77; C6 71.48; C12 130.74; C13 126.12; C14 131.18; C15 125.93; C16 34.23; C17 135.42.51; C18 117.79. MALDI-TOFMS: *m/z* 465 (M + 1). Anal. Calcd. for $C_{26}H_{28}N_2O_4S$: C, 67.24; H, 6.07; N, 6.03; S, 6.90. Found: C, 67.11; H, 6.08; N, 5.94; S, 6.88.

Macrocycle 6. mp 128°C; yield 27%; 8.44 (d, J = 7.8 Hz, 2H), 7.85 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 6.85 (d, J = 16 Hz, 2H), 6.04 (m, 2H); 4.10 (m, 4H), 3.93 (m, 4H), 3.56 (s, 4H); 1.78 (d, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm) C1 167.41; C2 117.27; C3 156.43; C4 74.84; C5 69.30; C6 71.33; C12 133.81; C13 125.35; C14 134.18; C15 126.63; C16 137.11; C17 124.51; C18 18.83. MALDI-TOFMS: *m/z* 465 (M + 1). Anal. Calcd. for $C_{26}H_{28}N_2O_4S$: C, 67.24; H, 6.07; N, 6.03; S, 6.90. Found: C, 67.09; H, 6.03; N, 5.98; S, 6.82.

Synthesis of macrocycle (7). A suspension of macrocyclic compound **6** (1 g, 2.15 mmol) in boiling water (100 mL) was prepared, to which sodium carbonate crystals (0.5 g) were added, and 4 g of finely powdered potassium permanganate (4 g) was slowly introduced. The mixture was heated under reflux until the purple color of the permanganate disappeared (1–4 h). After cooling, the mixture was filtered to remove any

excess of manganese dioxide and carefully acidified with hydrochloride acid. The crude product was filtered, washed with water, and recrystallized from ethanol. mp 258°C; yield 47%; 11.31 (s, OH, 2H), 7.57 (d, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 6.98 (t, $J = 16$ Hz, 2H); 4.15 (m, 4H), 3.58 (s, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm) C1 167.77; C2 117.27; C3 157.11; C4 72.52; C5 69.43; C6 72.01; C12 134.6; C13 127.16; C14 135.75; C15 127.12; C16 163.67. MALDI-TOFMS: *m*/*z* 473 ($M + 1$). Anal. Calcd. for $C_{22}H_{20}N_2O_8S$: C, 55.93; H, 4.27; N, 5.93; S, 6.79. Found: C, 56.10; H, 4.30; N, 6.06; S, 6.74.

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