Silver(I) N-heterocyclic carbene-bridged calix[4]arene analogues as efficient [60]fullerene receptors†

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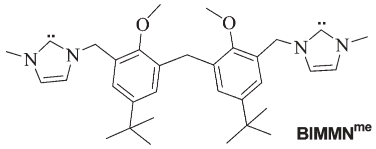
Two silver(I) N-heterocyclic carbene-bridged calix[4]arene analogues 4 and 5 were synthesized by a fragment-coupling approach; the preliminary inclusion properties of 5 with [60]fullerene shows that it is a novel efficient [60]fullerene fluorescent sensor.

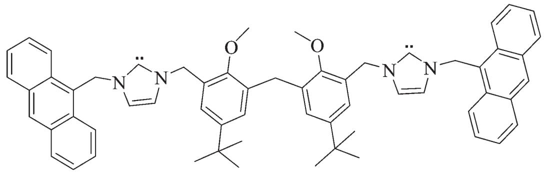
Calixarenes are a large and mature family of macrocyclic receptors,[1] which possess the merits of crown ethers and cyclodextrins.[2] These supramolecules contain a central annulus which is largely aromatic in nature, and are typically substituted on the upper- or lower-rim of the annulus, resulting in all kinds of host compounds for a wide range of guests. Up to date, the majority of calixarene hosts documented are cation hosts. Most of calixarene hosts have been designed as cation sensors, such as sodium, calcium, lead, silver and mercury.

Benefiting from their three-dimensional structure and the practical preorganized nature of the host cavity, these hosts have also been designed as hosts of fullerene families since Atwood *et al.*[3] and Shinkai *et al.*[4] indepently discovered the selective formation of a sparingly soluble C60/*p*-*t*-Bu-calix[8]arene complex in toluene in 1994. By the utilization of concave/convex complementarity principle, calix[*n*]arenes,[5] bis- and polycalix[*n*]arenes,[6] homooxacalix[3]arene,[7] azacalix[*m*]arene[*n*]pyridines[8] have been designed as efficient [60]fullerene receptors. Here, we report a conceptually new strategy to efficiently produce a new generation of calixarenes analogues by silver N-heterocyclic carbene (NHC) bridges, *viz.* complexes **4** and **5** which are formally formed by carbene ligands BIMMN^{me} and BIMMN$^{9\text{-anthrylme}}$ with silver cations and also can be considered as a special class of silver NHC based macrocycles.[9] The preliminary inclusion property of **5** with [60]fullerene is also investigated. A similar attempt to prepare P–Cu(I)–P bridged calix[4]arene analogues with inclusion ability for anions ClO_4^- and BF_4^- has been successfully completed by us.[10]

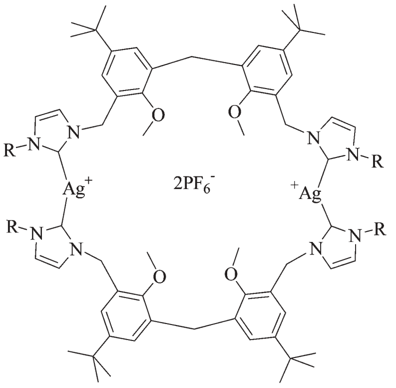
Silver carbene-bridged calix[4]arenes **4**‡ and **5** were prepared according to Scheme 1. Treatment of bis(3-bromomethyl-5-*tert*-butyl-2-methoxyphenyl)methane (**1**) with *N*-methylimidazole or *N*-(9-anthrylmethyl)imidazole in refluxing THF gave the hygroscopic bis[3-(*N*-methylimidazol-2-yl)methyl-5-butyl-2-methoxyphenyl]-methane chloride or bis[3-(*N*-(9-anthrylmethyl)imidazol-2-ylidene)methyl-5-butyl-2-methoxyphenyl]methane chloride which were converted to stable [H_2BIMMN^{me}]$(PF_6)_2$ (**2**) and [H_2BIMMN$^{9\text{-anthrylme}}$]$(PF_6)_2$ (**3**) by anion exchange with NH_4PF_6 in methanol in high yields. Reaction of **2** or **3** with silver oxide in DMSO afforded the bisilver carbene-bridged calix[4]arenes analogues **4** and **5** in good yield.



BIMMN^{me}

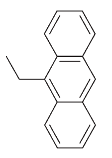


BIMMN$^{9\text{-anthrylme}}$

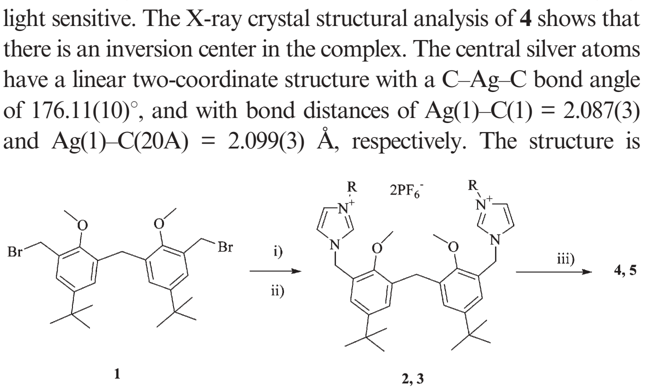


4 : R = CH$_3$

5: R =



Diffusion of ether into a acetonitrile solution of **4** afforded colourless crystals of **4**,§ which was stable in the air and slightly light sensitive. The X-ray crystal structural analysis of **4** shows that there is an inversion center in the complex. The central silver atoms have a linear two-coordinate structure with a C–Ag–C bond angle of 176.11(10)°, and with bond distances of Ag(1)–C(1) = 2.087(3) and Ag(1)–C(20A) = 2.099(3) Å, respectively. The structure is



Scheme 1 Syntheses of the macrocyclic receptors **4** and **5**. Reagents and conditions: (i) *N*-alkylimidazole, THF, refluxing for 2 days; (ii) methanol, NH_4PF_6; (iii) Ag_2O, DMSO, 75 °C, 12 h.

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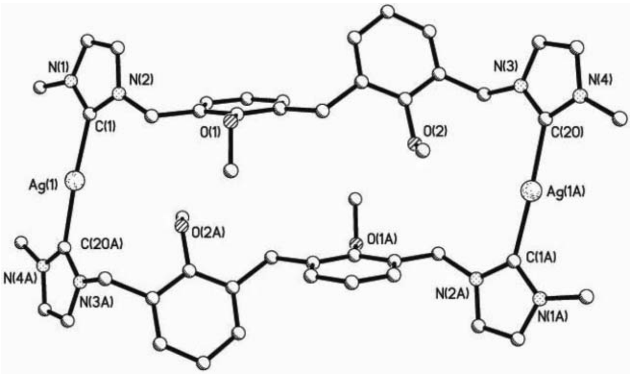

Fig. 1 X-Ray crystal structure of **4**. For clarity, all the hydrogens, the disordered *tert*-butyl carbon and anions are omitted. The additional "A" letters in the atom labels indicate that these atoms are at equivalent position (3/2 − *x*, 3/2 − *y*, 2 − *z*).

shown in Fig. 1. The dihedral angles of two imidazolium rings coordinated to the same metal atoms are 10.0°. The intramolecular separation of Ag(1)–Ag(1A) is 13.715 Å. The four *p-tert*-butyl anisole moieties are in a 1,2-alternate comformation according to the assignment of calixarene structures. The four anisole methyls pointed to the cavity of the complex.

It is interesting to note that **4** forms an infinite linear aggregate as shown in Fig. 2. The molecules are π-stacked (interplanar distance of 3.55 Å) with head-to-tail interactions between each other. There are two independent imidazole rings and pairs of these rings related by twofold symmetry are what gives rise to pairs of π–π interactions. The five-membered ring with N1 and N2 makes a π–π interaction with the same ring at equivalent position (1 − *x*, *y*, 3/2 − *z*) with a 4.02 Å centroid···centroid separation, a 3.52 Å perpendicular distance and a 1.5° angle between the two rings. For the other five-membered ring with N3 and N4, the corresponding data values are symop (2 − *x*, *y*, 5/2 − *z*), centroid···centroid 3.94 Å, perpendicular distance 3.62 Å, and interplanar angle 3.9°.[11] It is interesting to note that this head-to-tail π–π interactions cause the Jacob's ladder shape aggregate as shown in Fig. 2. This type of self-assembly lead to intermolecular weak Ag–Ag contacts and interamolecular Ag–Ag distance of 3.77 Å, which is shorter than that (3.81 Å) in $[Ag(L)_2]_2[CF_3SO_3]_2$ (L = 1,3-bis(4-pyridyl)tetramethyldisiloxane).[12]

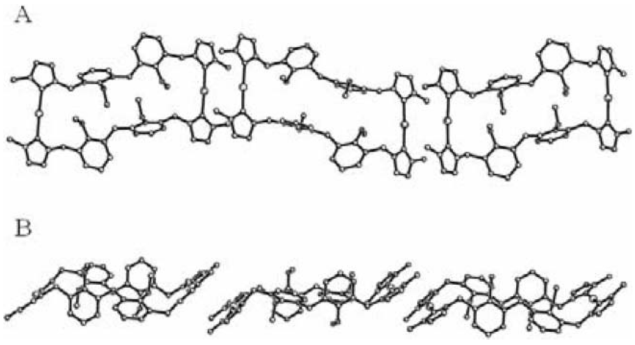

Fig. 2 A ladder-shape aggregate of **4** *via* parallelly-displaced π–π interactions of the carbene complex center. A: top-view and B: side view of the self-assemblies. For clarity, all the hydrogens and the disordered tert-butyl carbon are omitted.

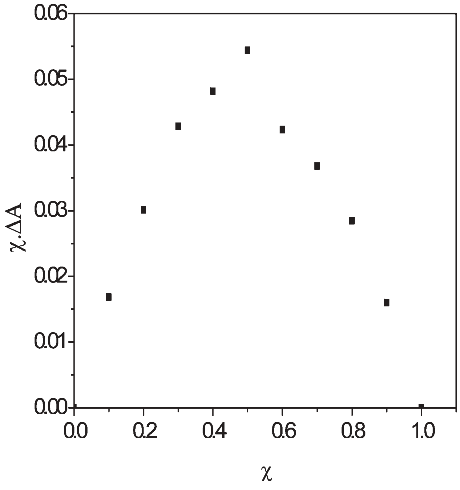

Fig. 3 The Job plot for $\mathbf{5}\cdot C_{60}$ complex in acetonitrile solution.

$[BIMMN^{9\text{-anthrylme}}]_2Ag_2(PF_6)_2$ (**5**) exhibits strongly [60]fullerene-complexation property. By means of the spectrophotometric measurement of a Job plot (375 nm)[13] upon mixing a solution of **5** and C_{60} in acetonitrile at 25 °C, the typical signature pattern of 1 : 1 complexation ($C_{60} \subset \mathbf{5}$) was observed, as shown in Fig. 3.

To further study the recognition of [60]fullerene by **5**, a fluorescence titration was conducted (Fig. 4). The fluorescence intensity of **5** at about λ_{em} = 425 nm decreased markedly with increasing concentration of [60]fullerene. The quenching is found to follow a Stern–Volmer equation and may be attributed to the charge transfer interaction between anthracene units and electron-deficient C_{60}. The stability constant K_s is 348 000 M^{-1}. To the best of our knowledge, this is the largest K_s value obtained up to date for complexation of [60]fullerene with a mono-macrocyclic receptor other than molecular clefts such as biscalix[*n*]arenes[6,14] and 'jaws porphyrins'.[15]

In summary, we have developed a fragment-coupling approach for the synthesis of silver N-heterocyclic carbene bridged calix[4]arene analogues. In the solid state, $[BIMMN^{me}]_2Ag_2(PF_6)_2$ (**4**) adopt a heavily twisted 1,2-alternate conformation with four methoxyls pointed in the void of the cyclic cavity, in which the bridging silver atoms conjugate with the neighboring imidazole

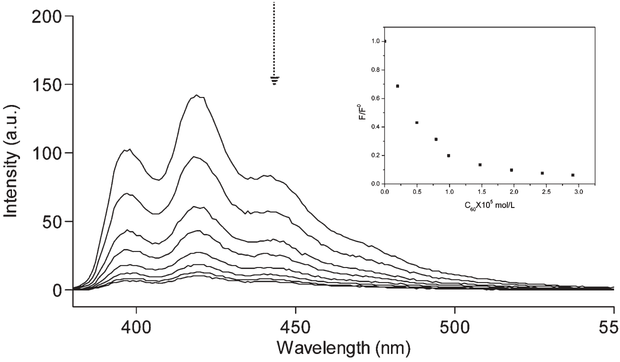

Fig. 4 Emission spectra (λ_{exc} = 370 nm) of **5** (1.01 × 10^{-5} mol L^{-1}) in the presence of C_{60} in acetonitrile at 25 °C. The concentrations of C_{60} for curves from top to bottom are 0.0, 0.204, 0.51, 0.816, 1.02, 1.53, 2.04, 2.55, 3.06 × 10^{-5} mol L^{-1}. Inset: Variation of fluorescence quenching F/F^0 of **5** with increasing C_{60} concentration.

carbene rings. We have also shown that [BIMMN$^{9\text{-anthrylme}}$]$_2$-Ag$_2$(PF$_6$)$_2$ (**5**) is a novel and efficient macrocyclic host molecule that complexes [60]fullerene in acetonitrile with a K_s value of 348 000 M^{-1} and acts as a good fluorescent sensor for [60]fullerene.

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Notes and references

‡ [BIMMN^{me}]$_2$Ag$_2$(PF$_6$)$_2$ (**4**). A 100 mL flask was charged with silver oxide (478 mg, 2.1 mmol), [H$_2$BIMMN^{me}](PF$_6$)$_2$ (**2**) (850 mg, 1.03 mmol) and DMSO (50 mL). The suspension was washed with nitrogen flow for 30 min and then heated to 75 °C for 12 h. The solution was filtered. The filtrate was diluted with water (100 mL) and the product precipitated imediately. The precipitate was collected by filtration, washed with small portions of cold ethyl ether. The product was purified by recrystallised from acetonitrile and ethyl ether. The product was obtained by filtration and dried in a vacuum to provided the pure product [BIMMN^{me}]$_2$Ag$_2$(PF$_6$)$_2$ (**4**) (610 mg) as an air- and moisture-stable and moderately light-sensitive white powder in 75% yield; mp > 250 °C; ^{1}H NMR (300 MHz, DMSO-d$_6$): 7.44 (s, 4 H), 7.42 (s, 4 H), 7.15 (s, 4 H), 6.96 (s, 4 H), 5.23 (s, 8 H), 3.81 (s, 12 H, –N–CH$_3$), 3.75 (s, 2 H, –CH$_2$–), 3.62 (s, 2 H, –CH$_2$–), 3.33 (s, 12 H, –OCH$_3$), 1.04 (s, 36 H, *t*-Bu). ^{13}C NMR (75 MHz, DMSO-d$_6$): 153.8, 146.28, 132.84, 129.01, 127.92, 124.94, 123.02, 122.97, 122.03, 121.97, 60.66, 49.98, 33.85, 30.81, 28.96. MS (SEI): 1423.23 (M–PF$_6$). Anal. Calcd. for $C_{67}H_{92}Ag_2F_{12}N_8O_4P_2$: C, 50.96; H, 5.87; N, 7.17%. Found: C, 50.87; H, 5.83; N, 7.21%.

§ Crystallographic details for [BIMMN^{me}]$_2$Ag$_2$(PF$_6$)$_2$ (**4**). A crystal of dimensions 0.24 × 0.18 × 0.16 mm^3 was mounted on a glass fiber in a random orientation. A total of 30 212 reflections ($-37 \leqslant h \leqslant 28$, $-23 \leqslant h \leqslant 23$, $-23 \leqslant h \leqslant 22$) were collected at T = 293(2) K in the range of 1.77–27.99°, of which 10 755 were unique (R_{int} = 0.0280); Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods. All non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriated isotropic thermal parameters, and included in structure factor calculations. The residual peak and hole of electron densities were 0.599 and −1.106 eA^{-3}. The absorption coefficient was 0.543 mm^{-1}. The least-squares refinement converged with residuals of $R(F)$ = 0.0433, $wR(F^2)$ = 0.1209, and a GOF = 0.970 [$I > 2\sigma(I)$]. $C_{66}H_{88}Ag_2F_{12}N_8O_4P_2$, space group C_2/c, monoclinic, a = 28.615(2), b = 17.5595(13), c = 17.8881(13), α = 90°, β = 90°, γ = 90°, V = 8987.9(12) A^3, Z = 4, ρ_{calcd} = 1.246 Mg m^{-3}. CCDC 619110. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612421f

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