

Chemical Communications

A self-complexing and self-assembling pillar[5]arene

Nathan L. Strutt,^{a,b} Huacheng Zhang,^a Marc A. Giesener,^a Juying Lei,^a J. Fraser Stoddart^{*,a,b}

^aDepartment of Chemistry, Northwestern University,2145 Sheridan Road, Evanston, IL, 60208-3113, USA.

^bGraduate School of EEWS (WCU), Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea.

* To Whom Correspondence should be Addressed	
Professor J Fraser Stoddart	
Department of Chemistry	1
Northwestern University	
2145 Sheridan Road	
Evanston, Illinois 60208-31	.13
Tel: (+1)-847-491-3793	
Fax: (+1)-847-491-1009	
E-Mail: stoddart@northwester	n.edu

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S1. General Methods

Reagents were purchased from Aldrich and were used without further purification. The mono-azido pillar[5]arene 1, N-(3-butynyl)-N'-methyl-4,4'-bipyridinium bis(hexafluorophosphate) (2), and 1,4dimethoxypillar[5]arene (S5) were prepared according to literature procedures.^{S1-3} Solvents (MeCN, CH₂Cl₂) were dried using a commercial solvent purification system (SG Water, Inc.) and H₂O was triply distilled. All reactions were performed under a nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was carried out using glass plates, precoated with silica gel 60 with fluorescent indicator (Whatman LK6F). Flash chromatography was carried out using silica gel 60 (Silicycle) as the stationary phase. UV Spectra were recorded with TU-1800pc UV-Vis Spectrophotometer at 298K, unless stated otherwise. K_a Values were calculated using Dynafit,^{S4} a program which employs nonlinear leastsquares regression analysis. Fluorescence measurements were recorded on a Shimadzu RF-5301 PC spectrofluorophotometer, using a quartz cell with degassed solvent at 298K. 1D and 2D nuclear magnetic resonance (NMR) spectra were recorded at 298 K, unless stated otherwise, on Bruker Avance III 500 and 600 MHz spectrometers, with working frequencies of 499.373 and 600.168 MHz for ¹H, and 125.579 and 150.928 MHz for ¹³C nuclei, respectively. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent (CDCl₃: 7.26 ppm), and coupling constants were recorded in Hertz (Hz). All ¹³C spectra were recorded with the simultaneous decoupling of proton nuclei. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; p, pentet; m, multiplet or overlapping peaks. Electrospray Ionization (ESI) mass spectra were obtained on an Agilent 6210 LC-TOF high-resolution mass spectrometer. SEM images were obtained on a FEI Quanta 600 SFEG scanning electron microscope (0.2-30 kV) equipped with both solid-state BSED and low vacuum LFSED as detectors. Optical microscopy images were recorded with an Olympus BX53 research microscope. DLS measurements were carried out with a Zetasizer Nano ZS instrument purchased from Malvern Instruments Ltd. at 298K using a 633 nm 'red' laser. The mean hydrodynamic radius was calculated with Zetasizer software. Viscosity measurements were conducted using a CannonUbbelohde Semi-Micro Viscometer in a 20°C water bath. Electrochemical experiments were carried out at room temperature with argon-purged solvents employing a Gamry Reference 600 potentiostat interfaced to a PC. Cyclic voltammetry was performed using a glassy carbon working electrode (0.071 cm², Cypress Systems). The counter electrode was a Pt coil and the reference electrode was a standard Ag/AgCl electrode. The concentration of the sample and supporting electrolyte (TBAPF₆) were 100 mM and 1 mM, respectively. Powder x-ray diffraction was collected on a Rigaku ATXG with Cu K α radiation ($\lambda = 0.15406$ nm, 50 kV, 240 mA).

S2. Compounds Synthesised



S3. Synthesis of New Compounds

3: A degassed solution of $[Cu(MeCN)_4]PF_6$ (4.6 mg, 0.012 mmol) and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (6.6 mg, 0.012 mmol) in MeCN (0.5 mL) was added to a degassed solution of**1**(0.100 g, 0.124 mmol) and*N*-(3-butynyl)-*N'*-methyl-4,4'-bipyridinium bis(hexafluorophosphate) (**2**) (0.083 g, 0.161 mmol) in Me₂CO (15 mL) under nitrogen atmosphere. The solution was stirred for 2 days at 30°C, before being concentrated under vacuum, and subjected to silica gel chromatography (gradient of CH₂Cl₂/MeCN/NH₄PF₆ from 100:0:0 to 0:99:1) to give**3** $(0.099 g, 60%). ¹H NMR (500 MHz, CD₃CN, 298 K, 1 mM) <math>\delta = 8.76$ (d, *J* = 7 Hz, 2H), 8.72 (d, *J* = 6 Hz, 2H), 8.12 (d, *J* = 7 Hz, 2H), 8.11 (d, *J* = 6 Hz, 2H), 7.69 (s, 1H), 6.88 (s, 1H), 6.87(1) (s, 1H), 6.86(7) (s, 1H), 6.86 (s, 2H), 6.85 (s, 1H), 6.83 (s, 1H), 6.79 (s, 1H), 6.74 (s, 1H), 6.67 (s, 1H), 4.97 (t, *J* = 6 Hz, 2H), 4.70 (t, *J* = 5 Hz, 2H), 4.38 (s, 3H), 4.15 (t, *J* = 5 Hz, 2H), 3.71–3.66 (m, 33 H), 3.57 (s, 2H), 3.46 (t, *J* = 7 Hz, 2H), 3.40 (s, 2H). ¹³C NMR (125 MHz, CD₃CN, 298 K) $\delta = 151.5$, 151.2, 151.1(5), 151.1(3), 151.1(0), 151.0(9), 151.0(4), 151.0(3), 150.5, 149.7, 149.3, 147.1, 146.7, 142.3, 129.7, 129.5(9), 129.5(7), 129.5(4), 129.5(3), 129.4(9), 129.4, 129.3, 129.0, 128.9, 127.5, 127.4, 124.6, 115.4, 114.2, 114.0(8), 114.0(5), 114.0(0), 113.9(8), 113.9, 67.9, 62.0, 56.5, 51.0, 49.5, 29.9, 29.7, 27.4. HRMS: (*m*/z): calcd for [*M* – PF₀]⁺: 1174.453; found 1174.457.

4: A degassed solution of $[Cu(MeCN)_4]PF_6$ (25 mg, 0.067 mmol) in MeCN (0.5 mL) was added to a degassed solution of *N*-(3-butynyl)-*N'*-methyl-4,4'-bipyridinium bis(hexafluorophosphate) (**2**) (100 mg, 0.195 mmol) and 1-azidohexane (480 mg, 3.78 mmol) in Me₂CO (15 mL) under nitrogen atmosphere. The solution was stirred for 2 days at 30°C, before being concentrated under vacuum, washed with hexanes and subjected to silica gel chromatography (gradient of CH₂Cl₂/MeCN/NH₄PF₆ from 100:0:0 to 0:99:1) to give **4** (70 mg, 56%). ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 8.86 (d, *J* = 7 Hz, 2H), 8.83 (d, *J* = 7 Hz, 2H), 8.34 (m, 4H), 7.60 (s, 1H), 4.97 (t, *J* = 7 Hz, 2H), 4.39 (s, 3H), 4.28 (t, *J* = 7 Hz, 2H), 3.42 (t, *J* = 7 Hz, 2H), 1.80 (p, *J* = 7 Hz, 2H), 1.26 (m, 6H), 0.86 (t, *J* = 7 Hz, 3H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 151.0, 150.4, 147.4, 146.8, 127.8, 127.7, 61.8, 51.1, 49.6, 31.8, 30.7, 27.9, 26.7, 23.1, 14.2. HRMS: (*m/z*): calcd for [*M* – PF₆]⁺: 496.2059; found 496.2065.

S4. NMR Spectroscopy



Figure S1. ¹H NMR spectrum (500 MHz, CD₃CN, 298K) of **3**.



Figure S2. 2D COSY NMR (500 MHz, CD₂Cl₂, 1.0 mM, 298K) spectra of 3.

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Figure S4. 2D NOESY NMR (500 MHz, CD₂Cl₂, 298K) spectra of 3.

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Figure S5. ¹H-¹³C HSQC NMR (500 MHz, CD₃CN, 298K) of **3**.



S7

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Figure S7. Variable temperature (VT) ¹H NMR (600 MHz, CD₂Cl₂, 0.1 mM) spectroscopy. All temperatures were calibrated using a MeOD standard and calibration curve. H₃ and H₄ separate into two distinct peaks. The self-complexation to decomplexation rate (k_c) was calculated using the Erying equation to be 228 s⁻¹ at the coalescence temperature (T_c) of 248 K, corresponding to an activation energy barrier (ΔG^{\ddagger}) of 11.8 kcal/mol.

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Figure S8. Variable Concentration ¹H NMR (500 MHz, CD_2Cl_2 , 298K) spectroscopy. All spectra were acquired within 15 min of preparing the sample to prevent gelation within the NMR tube.

S5. UV-Vis Spectroscopy



Figure S9. Comparison of the UV-vis spectra of **3** in several different solvents (5 mM, CH_2Cl_2 , MeCN, Me_2CO) Inset: Image of the samples (AC = Me_2CO, MeCN, D = CH_2Cl_2).



Figure S10. Variable Temperature UV-Vis spectra of **3** in CH_2Cl_2 (Purple = 0°C; green = 10°C; red = 20°C; 30°C).



Figure S11. Maximum λ (nm) of absorption of **3** in CH₂Cl₂ over a range of concentrations.

S6. Determination of K_a Value and Complex Stoichiometry

The association constant (K_a) between DMpillar[5]arene (**S5**) and modified viologen (**S4**) was determined through a fluorescence quenching titration experiment in order to compare the K_a to previously reported values for similar complexes.^{S3} As fluorescence quenching experiments often give a falsely high K_a value, the K_a was also determined using a UV-vis spectroscopic titration.



Figure S12. Fluorescence spectroscopy (Ex. $\lambda = 279$ nm, Em. $\lambda = 325$ nm) titration of a solution of **S4** (5 mM, 96:4 CH₂Cl₂/MeCN) into a solution of **S5** (100 μ M, 96:4 CH₂Cl₂/MeCN). Three trials were conducted and a K_a value of $1.3 \pm 0.2 \times 10^5$ M⁻¹ was calculated using Dynafit.^{S4}



Figure S13. Job Plot of the complex formed between **S4** and **S5** showing a 1:1 stoichiometry. Fluorescence spectroscopy (Ex. $\lambda = 279$ nm, Em. $\lambda = 325$ nm, 100 μ M, 96:4 CH₂Cl₂/MeCN). The gaussian line is meant to act as a visual aid.



Figure S14. UV-vis spectroscopic titration of a solution of **S4** (20 mM, 1:1 CH₂Cl₂/MeCN) into a solution of **S5** (2 mM, 1:1 CH₂Cl₂/MeCN). Using the absorbance at 345 nm, a K_a value of $3.3 \pm 0.7 \times 10^3$ M⁻¹ was calculated using Dynafit.^{S4} Because of the low solubility of **S4** in CH₂Cl₂ at concentrations needed for UV-vis spectroscopy, this K_a determination could not be completed under the same conditions as the fluorescence spectroscopic titration.

S7. Cyclic Voltammetry Experiments



Figure S15. CV (200 mVs⁻¹, 1 mM in Me₂CO, 100 mM TBAPF₆) of **2** (blue) and **3** (red).

S8. Dynamic Light Scattering Experiments



Figure S16. DLS measurements of solutions of 3 in CH_2Cl_2 over a range of concentrations. Molecular modelling (MMFF94) of the acyclic trimer and tetramer reveals that the length of these species is similar to the r_h values reported by DLS measurements.

S9. Viscosity Measurements



Figure S17. Double logarithmic scaled plot of concentration (mM) and specific viscosity (η_{sp}). Linear equations for the regions of 0.5 to 15 and 15 to 30 mM are shown on the plot with corresponding R² values.

S10. SEM Images of Gel



Figure S18. Additional SEM images of gel formed by 3 in CH₂Cl₂.

S11. X-Ray Powder Diffraction (XRD) Measurements

The X-ray powder diffraction (XRD) pattern of a sample of dried **3** (Figure S19) shows sharp reflections, indicating that the sample is in a crystalline state, while the XRD pattern for **3** in a gel state (Figure S20) shows very weak reflections and sharp crystalline diffraction peaks.



Figure S19. XRD pattern of a dried sample of 3.



Figure S20. XRD pattern of a dried gel formed from 3.

S12. References

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