Supporting information

Cucurbit[7]uril as "Protective Agent": Controlling Photochemistry and Determining 1-Adamantanamine

Hui Yang, Yiliu Liu, Liulin Yang, Kai Liu, Zhiqiang Wang and Xi Zhang*

Key Lab of Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

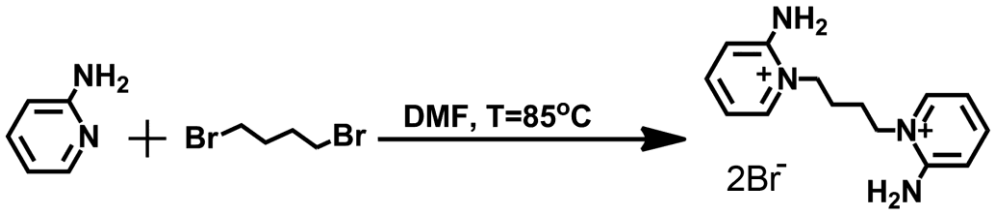
1. Experimental Section

1.1 Material

Cucurbit[7]uril (CB[7]) was prepared according to the literature.[1] 2-Aminopyridine (98%), bromoethane (98%) and 1,4-dibromobutane (99%) were received from ACRO.

1.2 Synthesis of 1,1'-(butane-1,4-diyl)bis(2-aminopyridine) bromide (DPAD)

1, 4-Dibromohexane (1.08 g, 0.005 mol) and 2-aminopyridine (1.88 g, 0.02mol) were dissolved in *N*, *N*-dimethylformamide (70 mL), and the mixture was stirred for 24 h at 85°C. The reaction solution was concentrated by rotary evaporation method and precipitated by the diethyl ether anhydrous and dried in vacuum to give DPAD (1.63 g, 81%). ^{1}H NMR (400MHz, D_2O, ppm) δ: 7.69 (m, 2H of 2-aminopyridine), 6.93 (s, H of 2-aminopyridine), 6.77 (s, H of 2-aminopyridine), 4.10 (s, 4H of butane), 1.82 (s, 4H of butane). ESI-MS: 122.03 (calcd: 122.03).



Scheme 1 Synthesis of DPAD

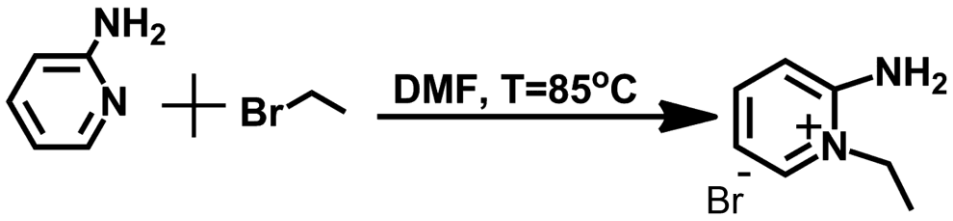
1.3 Synthesis of stable host-guest complex DPAD/CB[7]

CB[7] (4.65 mg, 4 μmol) and DPAD (1.61 mg, 4 μmol) were added into 2 mL D_2O,

and stirred for 12h at room temperature, which is used for photochemistry and ^{1}H NMR. ^{1}H NMR (D_2O, 400 MHz, ppm) δ: 7.61 (t, H of 2-aminopyridine), 7.44 (d, H of 2-aminopyridine), 6.71 (d, H of 2-aminopyridine), 6.64 (t, H of 2-aminopyridine), 5.68 (d, 14H from CB[7]), 5.53 (s,14H from CB[7]), 4.16 (d, 14H from CB[7]), 3.96 (s, 4H of butane), 1.72 (s, 4H of butane).

1.4 Synthesis of model molecule 2-amino-1-ethylpyridine (AED)

Bromoethane (0.545 g, 0.005 mol) and 2-aminopyridine (1.88 g, 0.02mol) were dissolved in *N*, *N*-dimethylformamide (50 mL), and the mixture was stirred for 24 h at 85^{o}C. The reaction solution was concentrated by rotary evaporation method and precipitated by the diethyl ether anhydrous and dried in vacuum to give AED (0.873 g, 86%). ^{1}H NMR (400MHz, D_2O, ppm) δ: 7.19 (m, 2H of 2-aminopyridine), 6.56 (s, H of 2-aminopyridine), 6.44 (s, H of 2-aminopyridine), 4.26 (s, 2H of ethyl), 2.06 (s, 3H of ethyl). ESI-MS: 123.4 (calcd: 123.4).



Scheme 2 Synthesis of AED

1.5 Synthesis of complex AED/CB[7]

CB[7] (4.65 mg, 4 μmol) and AED (0.81 mg, 4 μmol) were added into 2 mL D_2O, and stirred for 12h at room temperature, which is used for photochemistry and ^{1}H NMR. ^{1}H NMR (D_2O, 400 MHz, ppm) δ: 7.01 (t, H of 2-aminopyridine), 6.75 (d, H of 2-aminopyridine), 6.26 (d, H of 2-aminopyridine), 6.20 (t, H of 2-aminopyridine), 5.50 (d, 14H from CB[7]), 5.34 (s,14H from CB[7]), 4.33 (d, 14H from CB[7]), 3.94 (s, 4H of ethyl), 1.81 (s, 4H of ethyl).

2 Characterizations

The ^{1}H NMR spectra were recorded on a JEOL JNM-ECA 400 (400 MHz). ESI-mass spectroscopy was carried out on a LTQ LC/MS apparatus. The size distribution of the aggregates was analyzed by a Malvern 3000HS Zetasizer using a monochromatic coherent He–Ne laser (633 nm) as the light source and a detector that detected the

scattered light at an angle of 90°. The fluorescence spectra were measured using a Hitachi F-7000 spectrofluorometer with a quartz cell (optical path length 1 cm). The slit (ex/em) width was 2.5nm/2.5nm and the emission wavelength was 300 nm. UV-Vis spectra were obtained using a HITACHI U-3010 Spectrophotometer. DOSY experiments were carried out with a BRUKER AVANCE600 NMR spectrometer. ITC experiments were carried out with a Microcal VP-ITC apparatus in water at 298.15 K. The photochemical reactions of DPAD and DPAD/CB[7] for the measure of UV-Vis spectra and fluorescence spectra were carried out by high-pressure mercury lamp (RW-UVA, China, 900 mW/cm), and the photochemical reactions of DPAD and DPAD/CB[7] for ^{1}H NMR spectra were carried out by high-pressure mercury lamp (PLS-LAM500, China).

3 The host-guest interaction between AED and CB[7]

A model molecule 2-amino-1-ethylpyridine (AED) was designed and prepared. The host-guest interaction between AED and CB[7] was studied by ^{1}H NMR (Figure S2). Compared with AED alone, ^{1}H NMR spectrum of AED with equal molar CB[7] (AED/CB[7]) shows that all of the signals of AED are upshifted due to the shielding effect of CB[7]. It indicates that AED and CB[7] can form 1:1 host-guest complex.

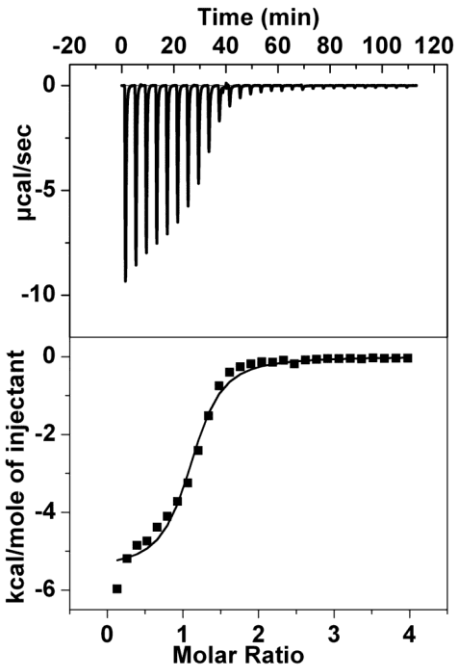


Fig. S1 ITC data for the titration of CB[7] (0.5 mmol/L) with DPAD

(5 mmol/L) in aqueous solution at 25 ^{o}C.

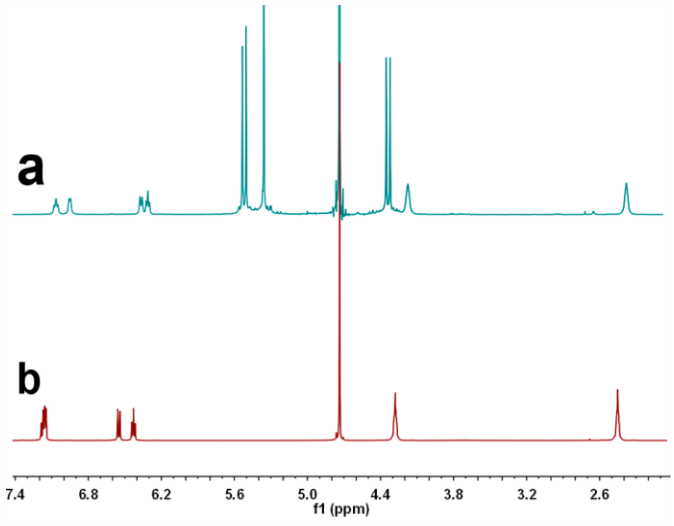


Fig. S2 ^{1}H NMR spectra of AED (b, 4 mmol/L) and host-guest complex AED/CB[7] (a, 4 mmol/L).

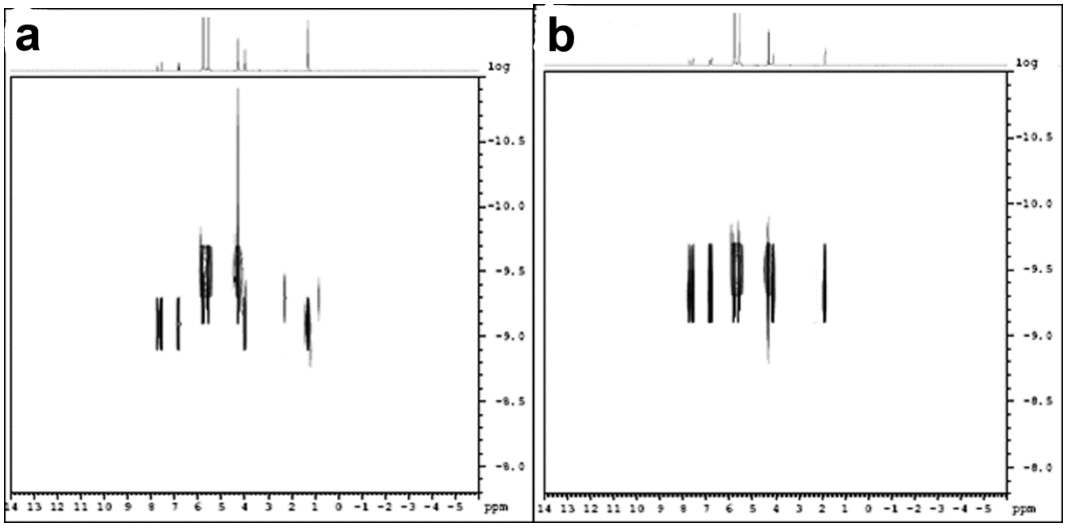


Fig. S3 Diffusion ordered spectroscopy (DOSY) of model molecule AED with the equal CB[7] (a) and DPAD with the equal CB[7] (b).

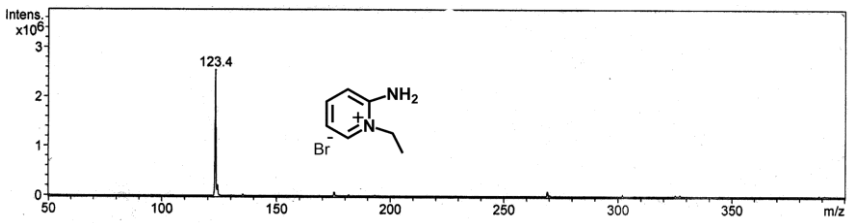


Fig. S4 ESI-MS of model molecule AED.

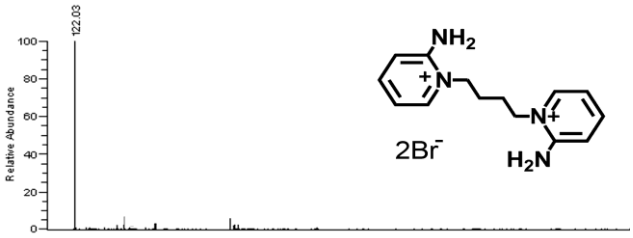


Fig. S5 ESI-MS of DPAD.

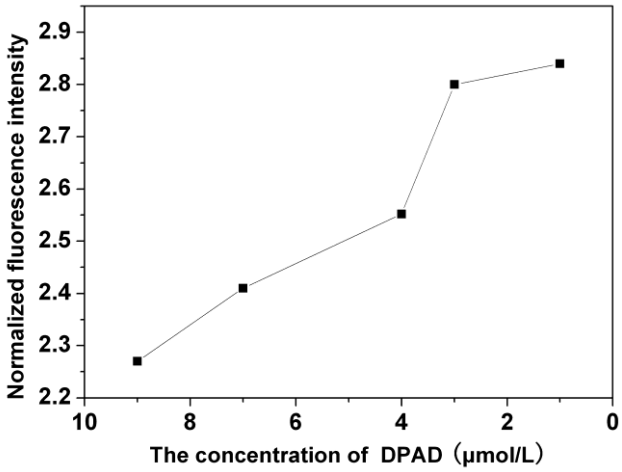


Fig. S6 The normalized fluorescence intensity curve of DPAD with increasing the concentration of DPAD

1 (a) A. Day, A. P. Arnold, R. J. Blanch, B. Snushall, *J. Org. Chem.* 2001, **66**, 8094; (b) J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* 2000, **122**, 540.