## SUPPORTING INFORMATION

## A cyanide-sensing detector in aqueous solution based on anion- $\pi$ interaction driven electron transfer

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## Instrumental methods

Reagents and solvents were purchased from Sigma-Aldrich, Alfa Aesar, and STREM and were used without further purification. Deuterated solvents were purchased from Euriso-TOP or Sigma-Aldrich and used without further purification.

Nuclear magnetic resonance spectra were recorded on a Bruker Ultra Shield 500 MHz and chemical shifts were expressed in ppm using TMS as an internal standard. Fluorescence spectra were obtained with a Shimadzu RF-5301 PC spectrophotometer with a quartz cuvette (path length = 1 cm). Absorption spectra were recorded using a Shimadzu 3100 UV-vis-NIR spectrophotometer. Mass spectra were obtained on Bruker MicroTOF (HRMS on Bruker MicroTOF-Q), with electrospray ionization. Nominal precision of the HRMS analysis is 10 ppm.

The EPR spectra were obtained on a JES-FA 200 EPR spectrometer.

Cyclic voltammetry (CV) experiments were performed on a BASi Epsilon potentiostat connected to a C3 standard electrochemical cell, consisting of a Pt gauche working electrode, Pt-wire counter electrode, and a Ag/AgCl reference electrode.



**Figure S1.** ESI-MS spectra of HAT(CN)<sub>6</sub> (1 mM, CH<sub>3</sub>CN) containing CN<sup>-</sup> (0.5 equiv.) at room temperature.



Figure S2. EPR spectra of HAT(CN)<sub>6</sub> (1 mM, CH<sub>3</sub>CN ) containing CN<sup>-</sup> (1 equiv.) at room temperature.



**Figure S3.** (a) UV-vis and (b) fluorescence spectroscopic changes of 50  $\mu$ M HAT(CN)<sub>6</sub> as a result of titration with various anions (200  $\mu$ M) in CH<sub>3</sub>CN. ( $\lambda_{ex} = 450$  nm)



**Figure S4.** (a) UV-vis spectroscopic changes of 50  $\mu$ M HAT(CN)<sub>6</sub> as a result of titration with CN<sup>-</sup> in a 1:1 CH<sub>3</sub>CN/H<sub>2</sub>O solution ([CN<sup>-</sup>] = 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1 equiv. of HAT(CN)<sub>6</sub>). (b) UV-vis absorption changes at 394 nm with increasing CN<sup>-</sup> concentrations in the range of 0-20  $\mu$ M.



**Figure S5.** UV-vis spectroscopic changes of 50  $\mu$ M HAT(CN)<sub>6</sub> as a result of titration with CN<sup>-</sup> in a 1:1 CH<sub>3</sub>CN/H<sub>2</sub>O solution ([CN<sup>-</sup>] = 1, 1.6, 2, 2.5, 3, 4, 6, 8 and 10 equiv. of HAT(CN)<sub>6</sub>).



**Figure S6.** Time course of the fluorescence intensity at 545 nm of 50  $\mu$ M HAT(CN)<sub>6</sub> with 6 equivalent of CN<sup>-</sup> in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1, v:v) solution at room temperature ( $\lambda_{ex} = 450$  nm).