Supporting Information for the article:

An Easily Accessible 3:1 Site-Differentiated [4Fe-4S] Cluster and Its Reaction with *p*-Fluorothiophenol

Erwin P. L. van der Geer,† Gerard van Koten,† Robertus J. M. Klein Gebbink,*† and Bart Hessen*†‡

†Chemical Biology & Organic Chemistry, Faculty of Science, Universiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands
‡Stratingh Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Synthesis and characterization of compounds 1 and 2.

Indole, thiourea, I_2, and KI were purchased from Acros and used as received. The synthesis of **2** was conducted under inert conditions using standard Schlenk techniques; solvents were flushed with N_2 before use.

3-Thiouroniumindole iodide (1). To a solution of indole (3.00 g, 25.6 mmol) and thiourea (1.95 g, 25.6 mmol) in a mixture of MeOH (80 mL) and water (20 mL) were added I_2 (6.50 g, 25.6 mmol) and KI (4.25 g, 25.6 mmol). After 3 days, the solution was concentrated to a black oil, which crystallized upon agitation. The product was washed with water and ether and recrystallized twice from acetone/diethyl ether. Yield: 7.17 g (22.5 mmol, 88%). Anal. Calcd for $C_9H_{10}IN_3S$: C, 33.87; H, 3.16; N, 13.17; S, 10.05. Found: C, 33.75; H, 3.08; N, 12.98; S, 10.07. ^{1}H NMR (DMSO-d_6): δ = 12.11 (s, broad, 1H, indolyl NH), 8.85 (s, broad, 2H, NH_2), 8.52 (s, broad, 2H, NH_2), 7.96 (d, $^3J_{H\text{-}H}$ = 2.7 Hz, 1H, indolyl H2), 7.55 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H, indolyl H), 7.50 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, indolyl H), 7.27 (td, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz, 1H, indolyl H), 7.21 (td, $^3J_{H\text{-}H}$ = 7.4 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz, 1H, indolyl H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 170.73 ($SC(NH_2)_2$), 136.79, 135.90, 128.26, 122.73, 121.03, 117.52, 112.77 (7 × indolyl C), 89.90 (indolyl CS). FT-IR (ATR, ν, cm^{-1}): 3288, 3250, 3132, 3090, 1689, 1637, 1607, 1457, 1425, 1412, 1342, 1284, 1237, 1127, 1042, 1008, 846, 739, 681.

Indole-3-thiol (2). A suspension of **1** (5.00 g, 15.7 mmol) in aqueous 2 M NaOH (60 mL) was heated to 100 °C for 15 min under constant stirring. After cooling to ambient temperature, the solution was filtered and aqueous 10 M HCl (12.5 mL) was added. A yellow precipitate formed, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated to a yellow, microcrystalline material. Yield: 2.14 g (14.4 mmol, 92%). Anal. Calcd for C_8H_7NS: C, 64.39; H, 4.73; N, 9.39; S, 21.49. Found: C, 64.27; H, 4.65; N, 9.20; S, 21.32. ^{1}H NMR (DMSO-d_6): δ = 11.25 (s, broad, 1H, NH), 7.56 (d, $^3J_{H\text{-}H}$ = 7.1 Hz, 1H, indolyl H), 7.43 (d, $^3J_{H\text{-}H}$ = 2.5 Hz, 1H, indolyl H2), 7.39 (d, $^3J_{H\text{-}H}$ = 7.1 Hz, 1H, indolyl H), 7.14 (td, $^3J_{H\text{-}H}$ = 7.2 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz, 1H, indolyl H), 7.08 (td, $^3J_{H\text{-}H}$ = 7.1 Hz, $^4J_{H\text{-}H}$ = 1.1 Hz, 1H, indolyl H), 4.23 (s, broad, 1H, SH). ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 136.16, 129.37, 128.83, 121.66, 119.26, 118.48, 111.76 (7 × indolyl C), 95.51 (CSH). FT-IR (ATR, ν, cm^{-1}): 3394, 3109, 3052, 2520, 1615, 1454, 1409, 1339, 1323, 1239, 1090, 1004, 930, 818, 740.