

*Supplementary Information*

**Detection of cyanide and sulfide ions by different mechanisms using a fluorescent chemical sensor containing a fluorophore and a potential ligand for metal complexes**

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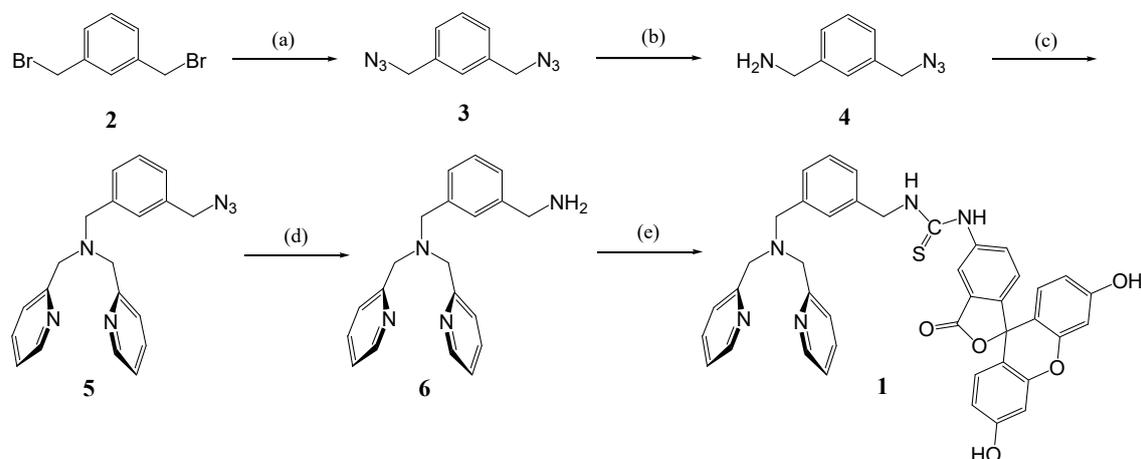
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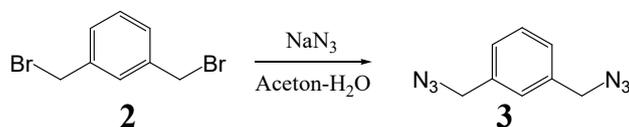
E-mail: [sslee0810@sch.ac.kr](mailto:sslee0810@sch.ac.kr)

## 1. Synthesis of compound 1 (BPMA-Flu)



(a)  $\text{NaN}_3$ , acetone-water (b)  $\text{Ph}_3\text{P}$  (1.0 eq), THF (c) 2-Chloromethylpyridine HCl (2.0 eq),  $\text{CH}_3\text{CN}$   
(d)  $\text{Ph}_3\text{P}$  (1.0 eq), THF (e) FITC, DMF

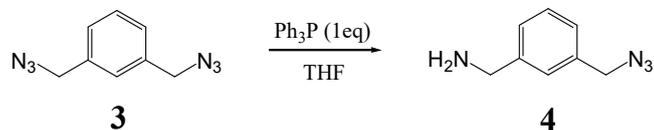
### (1) Synthesis of 1,3-Bis(azidomethyl)benzene, compound 3



To a stirred solution of compound 2 (5.30g, 20.0 mmol) in 50 mL acetone was added sodium azide (2.90g, 44.0 mmol) in 20 ml water. The reaction mixture was stirred overnight. The completion of the reaction was confirmed through TLC, after which the product (compound 3) was extracted with ethyl acetate (20 mL x 3). The organic layer was washed with brine (20 mL x 2). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure to obtain corresponding diazide compound 3 as a colorless oil (7.94g, 96% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.60 (4H, s), 6.86 (1H, s), 6.87 (2H, d), 7.04 (1H, t)

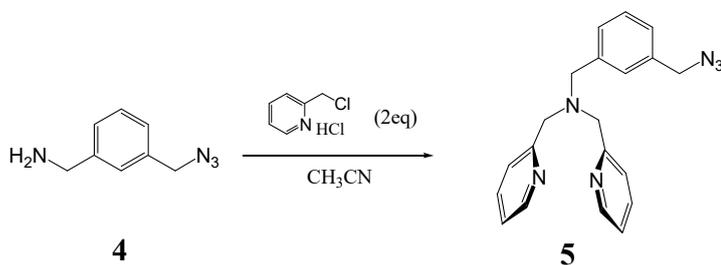
## (2) Synthesis of compound 4



Triphenylphosphine (2.62g, 10.0 mmol) in 30 ml THF was dropwise added to a stirred solution of compound 3 (3.76g, 20.0 mmol) in 50 mL THF at room temperature. The reaction was left to stir at room temperature for 24 h, after which it was quenched by the addition of water (10 equiv) and stirred for 2 h. The completion of the reaction was confirmed through TLC, after which the solvent was removed under reduced pressure. The residue was extracted with ethyl acetate (20 mL x 3). The organic layer was washed with brine (20 mL x 2). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel. Elution of 10% ethyl acetate-hexane gave product 4 as a colorless oil (2.98g, 92% yield).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.36 (4H, s), 6.86 (1H, s), 6.87 (2H, d), 7.04 (1H, t)

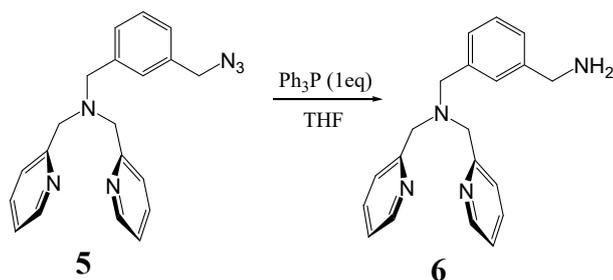
## (3) Synthesis of compound 5



To a stirred solution of 2-(chloromethyl)pyridine hydrochloride (6.15g, 37.5 mmol) and potassium carbonate (5.18g, 37.5 mmol) in 100 mL acetonitrile was dropwise added compound 4 (2.43g, 15.0 mmol) in 50 ml acetonitrile. The reaction mixture was stirred under

reflux overnight. The completion of the reaction was confirmed through TLC, after which the solvent was removed under reduced pressure. The residue was extract with dichloromethane (50 mL x 2). The organic layer was washed with water (50 mL x 2) and brine (50 mL x 2). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel. Elution of 5% methanol-dichloromethane gave product 4 as a colorless oil (2.69g, 52% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.71 (2H, s), 3.82 (4H, s), 4.33 (2H, s), 7.13-7.16 (3H, m), 7.33-7.39 (3H, m), 7.57 (2H, d), 7.66 (2H, t), 8.52 (2H, d)

#### (4) Synthesis of compound 6

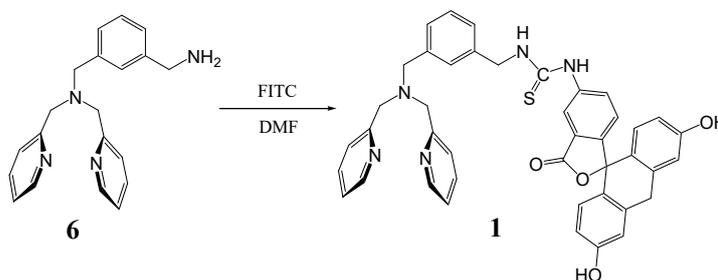


Triphenylphosphine (0.79g, 3.0 mmol) in 20 ml THF was dropwise added to a stirred solution of compound 5 (1.72g, 5.0 mmol) in 30 mL THF at room temperature. The reaction was left to stir at room temperature for 24 h, after which it was quenched by the addition of water (10 equiv) and stirred for 2 h. The completion of the reaction was confirmed through TLC, after which the solvent was removed under reduced pressure. The residue was extract with dichloromethane (30 mL x 2). The organic layer was washed with water (30 mL x 2) and brine (30 mL x 2). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel. Elution of 10% methanol-dichloromethane gave product 4 as a

colorless oil (1.47g, 92% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.74 (2H, bs), 3.69 (2H, s), 3.80 (4H, s), 3.86 (2H, s), 7.13-7.33 (6H, m), 7.58-7.67 (4H, m), 8.51-8.53 (2H, m)

### (5) Synthesis of compound 1



Fluorescein isothiocyanate (0.39g, 1.0 mmol) was added to a stirred solution of compound 6 (0.32g, 1.0 mmol) in 30 mL DMF at room temperature. The reaction was left to stir at room temperature for 24 h. The completion of the reaction was confirmed through TLC, after which 50 mL of diethyl ether was added to the reaction mixture to form a precipitate. The precipitate formed was filtered, washed with diethyl ether several times and dried under reduced pressure. The orange-yellow precipitate was collected. (0.56g, 78% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.40 (2H, s), 3.42 (2H, s), 3.67 (2H, s), 3.73 (4H, s), 4.81 (2H, bs), 6.56-6.60 (5H, m), 6.67 (2H, d), 7.18-7.24 (6H, m), 7.32 (2H, s), 7.49 (1H, s), 7.62 (2H, d), 8.26 (1H, s), 8.47 (2H, d), 8.57 (1H, bs), 10.11 (1H, bs)

## 2. Job's plot for BPMA-Flu-Cu<sup>2+</sup>

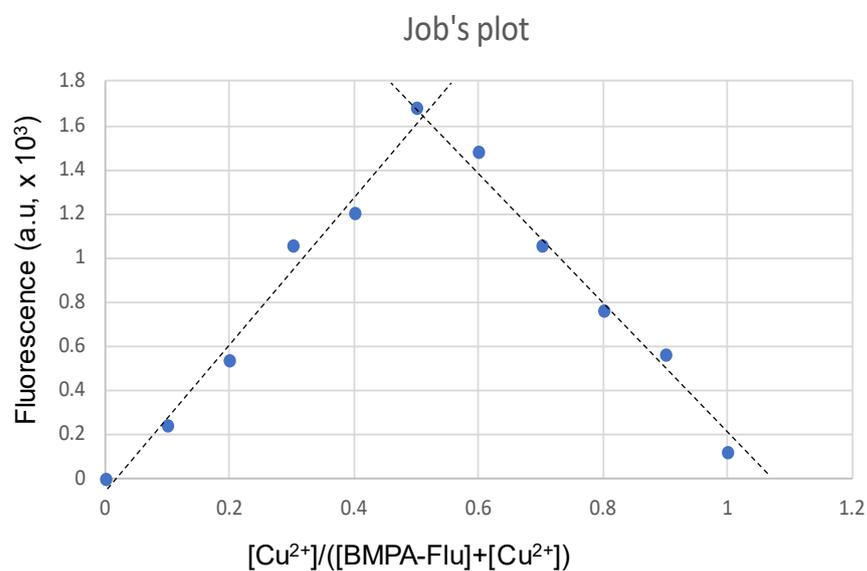


Fig. S1. Job's plots of the complexation between BPMA-Flu and Cu<sup>2+</sup>. Total concentration of BPMA-Flu + Cu<sup>2+</sup> was kept constant at 5.0  $\mu$ M.

## 3. Job's plot for DMA-Flu-Cu<sup>2+</sup>

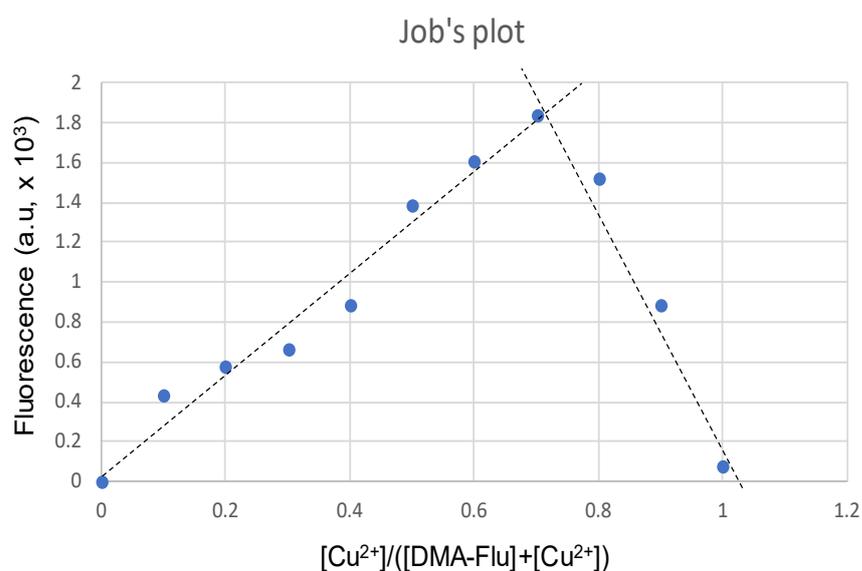
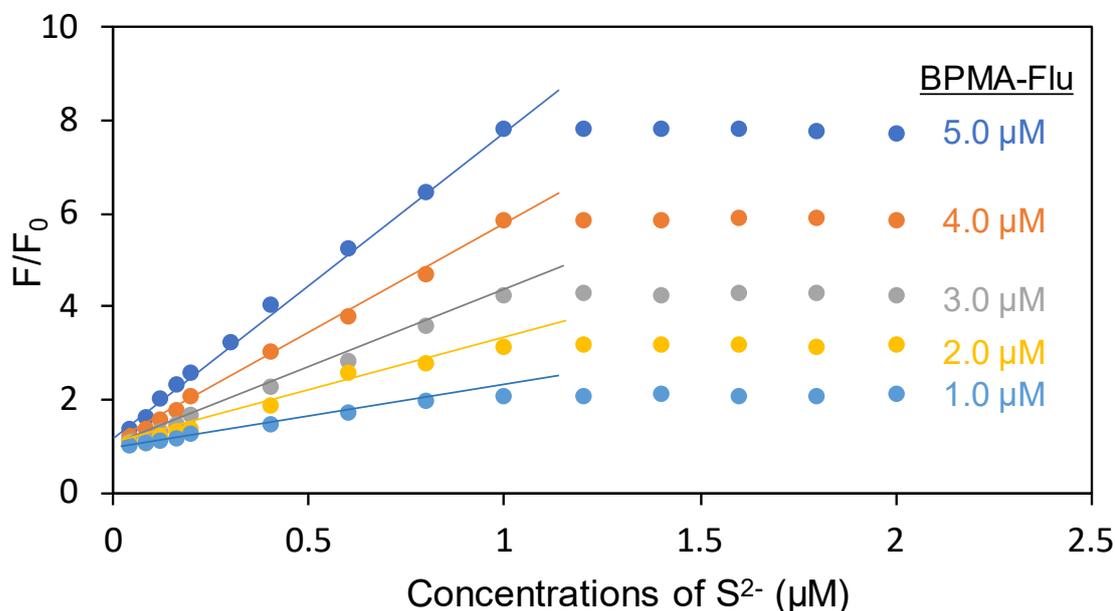


Fig. S2. Job's plots of the complexation between DMA-Flu and Cu<sup>2+</sup>. Total concentration of DMA-Flu + Cu<sup>2+</sup> was kept constant at 5.0  $\mu$ M.

#### 4. Optimization of BPMA-Flu concentration



**Fig. S3** Change in the RFU ratios ( $F/F_0$ ) of the BPMA-Flu-Cu<sup>2+</sup> complex (1.0 to 5.0 μM) by the addition of different concentrations of S<sup>2-</sup> ions.  $F_0$  and  $F$  mean the initial RFU value and RFU value after addition of S<sup>2-</sup> ions, respectively.

#### 5. Comparison of several CN<sup>-</sup> and S<sup>2-</sup> ions sensing technologies

Table S1. Comparison of several CN<sup>-</sup> and S<sup>2-</sup> ions sensing technologies.

Analytical techniques	Linear dynamic range (μM)	LODs (μM)	References
<b>[CN<sup>-</sup>]</b>			
Colorimetry (CAX-CN)	0.0015 - 0.78	0.00031	[1]
Colorimetry (Cyanocobalamin)	-	4.15	[2]
Fluorescence (Shiff-based compound)	-	0.057	[3]
Fluorescence (Thiadiazole compound)	0.1 - 1,500	210	[4]
Fluorescence (Benzimidazole)	-	0.0094	[5]
Fluorescence (BPMA-Flu)	0.1 - 200	0.29	This work

[S <sup>2-</sup> ]			
Colorimetry (Coumarin probe)	-	60	[6]
Colorimetry (Carrageenan-Silver)	2.5 - 1,000	1.7	[7]
Colorimetry (ABTS with Au)	0.5 - 15	0.28	[8]
Fluorescence (Carbon dots)	0.1 - 10	0.0023	[9]
Fluorescence (ZnMOF)	0.002 - 90	0.0065	[10]
Fluorescence (Fluorescein-DPA)	-	0.42	[11]
Fluorescence (BPMA-Flu)	0.1 - 5	0.074	This work

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