# Fluorescent <br> and electrochemical supramolecular coordination polymer hydrogels formed from ion tuned self-assembly of small bis-terpyridine monomer 

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Scheme S1 the synthesis procedure of DTA

Synthesis of $\mathbf{1}$ could be seen in literature 36 in the MS.
Synthesis of 2
Compound $\mathbf{1}(1.16 \mathrm{~g}, 3 \mathrm{mmol})$ and trimethylsilylacetylene ( $0.3 \mathrm{~g}, 3 \mathrm{mmol}$ ), $\mathrm{CuI}(0.03 \mathrm{~g})$, $\mathrm{Pd}(\mathrm{PhP})_{3} \mathrm{Cl}_{2}(0.12 \mathrm{~g})$ were refluxed in THF $(60 \mathrm{~mL})$ for 48 hours, then the reaction mixture was concentrated and purified by column chromatography (dichloromenthane/methanol, $10 / 1, \mathrm{v} / \mathrm{v}$ ), pale yellow solid was obtained ( 0.97 g , yield
$80 \%$ ). Mp: $150-152{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{M}, \mathrm{CDCl}_{3}, \delta$ ): 0.284 (s, 9 H ), 7.35-7.38 (t, 2 H , $\mathrm{J}=5.5 \mathrm{~Hz}$ ), $7.60-7.62(\mathrm{~d}, 2 \mathrm{H}, \mathrm{J}=8.5 \mathrm{~Hz}), 7.86-7.91(\mathrm{~m}, 4 \mathrm{H}), 8.67-8.68(\mathrm{~d}, 2 \mathrm{H}, \mathrm{J}=8 \mathrm{~Hz})$, 8.73-8.75 (m, 4H). ${ }^{13}$ CNMR (125 M, DMSO- $d_{6}$ ): 118.7, 118.8, 121.5, 124.0, 127.2, 129.0, 132.2, 132.6, 137.0, 149.3, 156.2, 156.3. MS calc. for $\left[\mathrm{C}_{26} \mathrm{H}_{23} \mathrm{~N}_{3} \mathrm{Si}+\mathrm{H}\right]^{+}$: 406.2; Found: 406.4 .

## Synthesis of 3

Compound $2(1 \mathrm{~g}, 2.47 \mathrm{mmol})$ and $\mathrm{K}_{2} \mathrm{CO}_{3}(5.5 \mathrm{~g})$ were stirred in solvent mixture ( 60 mL THF and $40 \mathrm{CH}_{3} \mathrm{OH}$ ) for two days, then the reaction mixture was concentrated and purified by column chromatography (dichloromenthane/methanol, 50/1, v/v), yellow solid was obtained ( $0.58 \mathrm{~g}, 70 \%$ ). Mp: $158-159{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{M}, \mathrm{CDCl}_{3}$, $\delta): 3.19(\mathrm{~s}, 1 \mathrm{H}), 7.34-7.37(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}=5.5 \mathrm{~Hz}), 7.63-7.64(\mathrm{~d}, 2 \mathrm{H}, \mathrm{J}=8.5 \mathrm{~Hz}), 7.86-7.89$ (m, 4H), 8.66-8.73 (m, 6H). ${ }^{13}$ CNMR ( 125 M , DMSO- $d_{6}$ ): 118.7, 121.4, 122.8, 123.9, 127.3, 128.9, 132.1, 132.7, 136.9, 138.8, 149.2, 156.1. MS calc. for $\left[\mathrm{C}_{23} \mathrm{H}_{15} \mathrm{~N}_{3}+\mathrm{Na}\right]^{+}$: 356.3; Found:356.2.

Synthesis of DTA
Compound $3(1 \mathrm{~g}, 3 \mathrm{mmol})$ and $\mathrm{Cu}(\mathrm{OAc})_{2}$ were heated at $60^{\circ} \mathrm{C}$ in pyridine for 20 h , then the reaction mixture was concentrated and washed with EDTA aqueous solution. The filtrate was finally purified by column chromatography (dichloromenthane/methanol, 30/1, v/v), yellow solid was obtained ( $0.65 \mathrm{~g}, 65 \%$ ). $\mathrm{Mp}: 299-300{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{M}, \mathrm{CDCl}_{3}, \delta$ ): 7.36-7.38 (t, $2 \mathrm{H}, \mathrm{J}=5.5 \mathrm{~Hz}$ ), 7.69-7.71 (d, $2 \mathrm{H}, \mathrm{J}=8.5 \mathrm{~Hz}$ ), 7.88-7.93 (m, 4H), 8.68-8.69 (d, 2H, J=8 Hz), 8.74-8.75 (m, $4 \mathrm{H}) .{ }^{13} \mathrm{CNMR}\left(125 \mathrm{M}\right.$, DMSO- $d_{6}$ ): 75.3, 81.9, 118.7, 121.4, 122.5, 124.0, 127.4, 133.1, 136.9, 139.3, 149.2, 156.1. MS calc. for $\left[\mathrm{C}_{46} \mathrm{H}_{28} \mathrm{~N}_{6}+\mathrm{Na}\right]^{+}: 687.7$; Found: 687,7.Anal. Calcd for: $\mathrm{C}_{46} \mathrm{H}_{28} \mathrm{~N}_{6}$ : C 83.11, H, 4.25, N 5.77; Found: C 83.10, H 4.28, N 5.74.


Figure S1. The room temperature gelation process of DTA upon the addition of $\mathrm{Cu}(\mathrm{OAc})_{2}$. a) 5 min ; b) 1 h ; c) 6 h ; d) 10 h .

Table S1 the gelation test of NSS ( $25 \mathrm{mg} / \mathrm{mL}$ ) in different solvents.

| Metal salts | Room temperature | Heating | Cooling |
| :---: | :---: | :---: | :---: |
| $\mathrm{ZnC}_{6} \mathrm{H}_{10} \mathrm{O}_{6}$ | 1 | S | G |
| $\mathrm{Zn}(\mathrm{ACO})_{2}$ | 1 | 1 | 1 |
| $\mathrm{ZnCl}_{2}$ | 1 | 1 | 1 |
| $\mathrm{ZnBr}_{2}$ | 1 | 1 | 1 |
| ZnI | 1 | 1 | 1 |
| $\mathrm{ZnF}_{2}$ | 1 | 1 | 1 |
| $\mathrm{CuI}_{2}$ | 1 | 1 | 1 |
| $\mathrm{Cu}(\mathrm{ACO})_{2}$ | G | 1 | 1 |
| Cupric lactate | 1 | 1 | 1 |
| $\mathrm{CuCl}_{2}$ | 1 | 1 | 1 |
| CuCl | 1 | 1 | 1 |
| $\mathrm{CdCl}_{2}$ | 1 | 1 | 1 |
| $\mathrm{Cd}(\mathrm{ACO})_{2}$ | 1 | 1 | 1 |


| $\mathrm{TbCl}_{3}$ | 1 | 1 | I |
| :---: | :---: | :---: | :---: |
| $\mathrm{Eu}\left(\mathrm{NO}_{3}\right)_{3}$ | 1 | 1 | I |
| $\mathrm{EuCl}_{3}$ | 1 | 1 | I |
| $\mathrm{Cr}\left(\mathrm{NO}_{3}\right)_{3}$ | 1 | 1 | I |
| $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{3}$ | 1 | 1 | I |
| $\mathrm{FeSO}_{4}$ | 1 | 1 | 1 |
| $\mathrm{AgNO}_{3}$ | 1 | 1 | 1 |
| $\mathrm{MnCl}_{2}$ | 1 | I | 1 |
| $\mathrm{Al}\left(\mathrm{NO}_{3}\right)_{3}$ | I | 1 | 1 |



Figure S2. Uv-vis spectra of DTA solution and DTA gels with $\mathrm{Zn}^{2+}$ and $\mathrm{Cu}^{2+}$ ions.


Figure S3. The photos of DTA gel and suspensions in light and in dark (irradiated by 365 nm ). From left to right: DTA/ $\mathrm{ZnC}_{6} \mathrm{H}_{10} \mathrm{O}_{6}$ (a), $\mathrm{ZnF}_{2}$ (b), $\mathrm{ZnCl}_{2}$ (c), $\mathrm{ZnBr}_{2}$ (d), $\mathrm{ZnI}_{2}$ (e), $\mathrm{Zn}(\mathrm{OAc})_{2}(\mathrm{f})$, Zinc gluconate (g), $\mathrm{Zn}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{~h}), \mathrm{ZnSO}_{4}$ (i).


Figure S4. SEM and TEM images of DTA $/ \mathrm{ZnC}_{6} \mathrm{H}_{10} \mathrm{O}_{6}$ hydrogel ( $25 \mathrm{mg} / \mathrm{mL}$ ). a) SEM image; b) TEM image; c) magnification picture of b). Scale bar: a) 500 nm , b) 20 nm , c) 10 nm .


Figure S5. TEM image of DTA/Cu(OAc $)_{2}$ hydrogel ( $25 \mathrm{mg} / \mathrm{mL}$ ). a) SEM image; b) TEM image; c) magnification picture of b). Scale bar: 100 nm .


Figure S6. TEM images of DTA/ $\mathrm{Zn}(\mathrm{OAc})_{2}$ assembly (a) and DTA/ Zinc gluconate assembly (b).


Figure S7. The gel to suspension and suspension to gel transition tuned by electrolysis process.


Figure S8. a) The electrolysis process of DTA at anode and cathode; b) the current changes of DTA hydrogel at cathode $v s$ time; c) the current changes of DTA hydrogel at anode.


Figure S9. The suspensions of $\mathbf{D T A} / \mathrm{Cu}(\mathrm{OAc})_{2}$ hydrogel upon the addition of EDTA (a) and KI.


Figure S10. a) CD spectra of DTA solution ( $2 \mathrm{mg} / \mathrm{mL}$ ) and the diluted DTA $/ \mathrm{Cu}(\mathrm{OAc})_{2}$ hydrogel assembly $(2 \mathrm{mg} / \mathrm{mL})$; b) CD spectra of $\mathbf{D T A} / \mathrm{Cu}(\mathrm{OAc})_{2}$ gels with different concentrations.


Figure S11. The CD spectra of DTA/Cu(OAc $)_{2}$ hydrogel $(25 \mathrm{mg} / \mathrm{mL})$ before and after irradiation of light.


Figure S12. The XRD spectra of DTA hydrogels.

