A supramolecular aggregation-based constitutional dynamic network for information processing

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1. DNA oligonucleotides used in this work

Sequence name	Sequence (5' to 3')	Bases
Code	GGTGGTGGTGGT	12 nt
Lock	GGGCGCGGGAGGAATTGGGCGGG	23 nt
Key	CCCGCCCAATTCCTCCCGCGCCCC	23 nt
Lock-2	TGAGGGTGGGGAGGGTGGGGAA	22 nt
Key-2	TTCCCCACCCTCCCCCCCCCC	22 nt

 Table S1 DNA oligonucleotides used in this work.

2. Synthesis and characterization of MTC

2.1 Synthesis of MTC



The cyanine dye *MTC* was synthesized according to the methods of Hamer^[1] and Ficken^[2]. In the first step, 0.51 g (2.56 mmol) 2-methylnaphthyl -thiazole and 1.05 g (8.59 mmol) 1,3-propyl sulfonate were mixed and reaction at 160 °C for 5 h. The reaction was traced with TLC. The mixture was then recrystallized in diethyl ether. After evaporated to dryness in vacuum 0.63 mg (77% yield) solid was obtained. Then 0.52 g solid (1.617 mmol), 0.53 g (3.267 mmol) triethyl orthoacetate, 1.05 g phenol (11.16 mmol) and 0.5 mL triethylamine were mixed and then heated at 120 °C for 1.5 h. When the reaction completed, ether was used to deal with the product and then methanol was used to recrystallization. After evaporated to dryness in vacuum 0.30 mg (25% yield) solid was obtained.

2.2 HRMS-ESI

*HRMS(ESI) m/z [M-H]⁻ = 665.09069

The calculated exact mass of $C_{32}H_{29}N_2O_6S_4$ is 665.09139.





2.3 ¹H-NMR spectrum - 5.00 12 11 | 11 Γ ł DMSO 13 g 2.00 -5.0 4.5 f1 (ppm) 10.0 9.5 9.0 8.5 8.0 7.0 6.5 6.0 5.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 10

Fig. S2 The ¹H-NMR spectrum of cyanine dye MTC in DMSO-d₆.

¹H NMR (600 MHz, DMSO- d_6) δ 8.65 (d, J = 8.7 Hz, 2H), 8.18 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H), 7.75 (t, J = 7.7 Hz, 2H), 7.66 - 7.63 (m, 2H), 6.80 (s, 2H), 5.06 - 4.97 (m, 4H), 3.10 - 3.05 (m, 8H), 2.91 (t, J = 6.6 Hz, 4H), 2.67 (s, 3H), 2.56 - 2.52 (m, 4H), 1.19 (d, J = 7.2 Hz, 12H).

According to the ¹H-NMR spectrum, the signals are in line with *MTC*'s structure but the integrations at 1.18 and 3.10 ppm show there are excessive triethylamine in the sample.

The signals at 1.18 and 3.10 ppm are assigned to the ethyl groups on the triethylammonium ion and the integration ratio (12:8) is in accordance with the triethylamine structure (3:2). Theoretically, the integrations at should be 9H (1.18 ppm) and 6H (3.10 ppm), respectively. However, in the synthesis process, the excessive triethylamine is difficult to eliminate completely. The excess signals may come from the residual triethylamine in the synthesis. Since small amount of triethylamine would not influence the feature of *MTC*, the sample was used without further purification.

2.4 ¹³C-NMR spectrum



Fig. S3 The ¹³C-NMR spectrum of cyanine dye *MTC* in DMSO-d₆.

¹³C NMR (151 MHz, DMSO-D6) δ 161.80, 156.31, 135. 82, 134.43, 130.42, 128.46, 127.08, 126.85, 124.95, 122.41, 122.06, 120.43, 100.98, 50.74, 48.67, 47.20, 25.52, 24.92, 9.23

2.5 HSQC and HMBC spectra



Fig. S4-B The HMBC spectrum of cyanine dye MTC in DMSO-d₆.

2.6 HPLC



Fig. S5 The HPLC trace of cyanine dye *MTC* in CH₃OH-H₂O solution (5-100% CH₃OH). Inertsil C₁₈ Column, flow rate 1.0 mL/min, T = 30 °C. (A)DAD:200-800 nm. (B) λ = 276 nm. (C) λ = 573 nm.

2.7 UV/Vis spectrum research and absorption coefficient calculation



Fig. S6 The absorption spectra of *MTC* monomer in methanol. Insert gives the curve of the absorbance at 573 nm against the concentration of *MTC* monomer.

Based on Lambert-beer's law, the molar absorption coefficient of MTC monomer is

 $\varepsilon^{M}_{1cm,573nm} = 1.00 \times 10^{6} M^{-1} \cdot cm^{-1}$

3. The quantity analysis of the constitutional distribution of the Agg-CDN

3.1 The calibration curves of the constitutions

Firstly, the D-band calibration curve was plotted via the change of the abosorbance at 515 nm with the experimental concentrations of *MTC* with 1 mM KCl (Fig. S7A). Then, the J-/H-bands (656 nm / 450 nm) calibration curves were obtained by correcting *MTC* concentrations on the basis of corresponding D-band intensity (Fig. S7B and C). The monomer calibration curve was plotted according to the fluorescence intensity at 612 nm without any correction (Fig. S7D).



Fig. S7 The calibration curves of Agg-CDN constituents: A) Monomer, B) Dimer, C) J-aggregates and D) H-aggregates.

Table S2. The linear-fitting results of the calibration curves of Agg-CDN constituents

MTC constituents	Monomer	Dimer	J-aggregates	H-aggregates
Fitted equation	FI=196.64c-28.07	Abs=0.04365c-0.02572	Abs=0.03066c-0.3962	Abs=0.05692c-0.04346
Linear range	0.2 - 1.0 μM	0.5 - 6.0 μΜ	1.35 - 3.5 μM	0.5 - 5.5 μΜ
Linear coefficient R ²	0.99651	0.99686	0.99161	0.99608

3.2 The calculation of constitution concentrations

Substituting the absorption intensity and fluorescence intensity at specific wavelengthes into the corresponding fitted equations to calculate the theoretical concentrations. The results were shown in Table S3. The calculated concentrations were summed by all four constituents are roughly equal to the experimental condition (6 μ M) (Fig. S8), inferring that the quantitative calculation could describe the constitutional balance of the Agg-CDN to some extent.

Concentration/µM	D!	T	II	M	G	
Agg-CDN state	Dimer	J-aggregates n-aggregates		Monomer	Summation	
S _D	6.06	0	0	0	6.06	
$\mathbf{S}_{\mathbf{J}}$	2.08	3.92	0	0	6.00	
$\mathbf{S}_{_{\mathrm{JH}}}$	1.54	1.92	2.56	0	6.02	
$\mathrm{S}_{_{\mathrm{H}}}$	1.54	1.36	3.20	0	6.10	
S _M	0	0	0	6.00	6.00	
S_{DM}	5.24	0	0	0.55	5.79	
$S_{_{JM}}$	2.21	3.02	0	0.84	6.07	
$\mathbf{S}_{_{\mathrm{JMH}}}$	1.42	1.68	1.80	0.98	5.88	
S_{MH}	1.54	1.50	1.96	1.00	6.00	
S _M	1.72	0	0	4.28	6.00	

Table S3 The absolute concentrations of each aggregates in every Agg-CDN states



Fig. S8 The histogram of the calculated concentrations of Agg-CDN constituents in nine Agg-CDN states.

4. Figures



Fig. S9 The absorption spectra (A) and the normalized absorbance (B) of 6 μ M *MTC* in 10 mM Tris-Ac buffer solution (pH 8.5) with the increasing KCl concentration from 0 mM to 60 mM.



Fig. S10 The absorption spectra (A) and the fluorescence spectra (B) of 6 μ M *MTC* in 1 mM KCl and various *Code* concentrations. (C) The absorbance of J-aggregates at 530nm and the fluorescence of monomer at 612nm change with the ratio of [*Code*] to [*MTC*].



Fig. S11 The absorption spectra (A) and the fluorescence spectra (B) of 6 μ M *MTC* in 10 mM KCl and various *Code* concentrations. (C) The absorbance of J-aggregates at 656nm and the fluorescence of monomer at 612nm change with the ratio of [*Code*] to [*MTC*].



Fig. S12 The absorption spectra (A) and the fluorescence spectra (B) of *MTC* in 60 mM KCl and various *Code* concentrations.
(C) The absorbance of J-aggregates at 656nm and the fluorescence of monomer at 612nm change with the ratio of [*Code*] to [*MTC*].



Fig. S13 Regulation the conversion bettween S_J and S_H by 18-crown-6 (CE) and KCl. (A) The absorption spectra in various coditions: a) 10 mM KCl (J-aggregates) b) 60 mM KCl (H-aggregates) c) 60 mM KCl and 50 mM CE (J-aggregates). (B) The normalized absorbance of J-aggregates in different states: a) 10 mM KCl b) 60 mM KCl c) 60 mM KCl and 50 mM CE.



Fig. S14 Regulation the conversion bettween S_J and S_M by the complementary DNA strand. (A) The absorption spectra in various coditions: a) 10 mM KCl (J-aggregates) b) 12 μ M *Lock* (Monomer) c) 12 μ M *Lock* and 14 μ M *Key* (J-aggregates). (B) The normalized absorbance of J-aggregates in different states: a) 10 mM KCl b) 12 μ M *Lock* c) 12 μ M *Lock* and 14 μ M *Key*.



Fig. S15 The kinetic curves of the constitutional dynamic conversions among constituents triggered by G4 DNA strand: (A) S_D to S_M (B) S_J to S_M (C) S_J to S_M .



Fig. S16 The panda logo for WWF as an example of encoding/decoding a black-and-white image via the Agg-CDN and the corresponding Agg-CDN states.



Fig. S17 The image units of the panda logo for WWF. (A) All image units of S_D (B) The absorption spectra of all S_D (C) The fluorescence spectra all S_D (D) All image units of S_J (E) The absorption spectra of all S_J (F) The fluorescence spectra all S_J .



Fig. S18 The image units of the panda logo for WWF. (A) All image units of S_{JM} (B) The absorption spectra of all S_{JM} (C) The fluorescence spectra all S_{JM} (D) All image units of S_{JMH} (E) The absorption spectra of all S_{JMH} (F) The fluorescence spectra all S_{JMH} .



Fig. S19 The image units of the panda logo for WWF. (A) All image units of S_H (B) The absorption spectra of all S_H (C) The fluorescence spectra all S_H (D) All image units of S_{DM} (E) The absorption spectra of all S_{DM} (F) The fluorescence spectra all S_{DM} (G) All image units of S_{MH} (H) The absorption spectra of all S_{MH} (I) The fluorescence spectra all S_{MH} .

	A	В	С	D	E	F
1			~			
2						
3						
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5						
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18						

Fig. S20 The absorption spectra of the panda logo for WWF.



Fig. S21 The fluorescence spectra of the panda logo for WWF.



Fig. S22 The absorption spectra of the encode (A), encrypyion (C) and decryption (E) of Sn. The fluorescence spectra of the encode (B), encrypyion (D) and decryption (F) of Sn.

J	M	Н	Agg-CDN states		Agg-CDN states	J	М	H
0	0	$0 0 \mathbf{S_p}$		Lock	S _M	Encryption		
1	0 0 S _J		S _J	37℃,90 min				
0	0	1	S _H					

The encryption operation

The decryption operation

Agg-CDN states	J	М	H		Intermediate state		Agg-CDN state	J	м	н
S _M				Key	للحم		S _D -	0	0	0
	Encryption	90°C, 5 min then cooling	2	37°C,90 min	SJ - J	1	0	0		
							S _H	0	0	1

Fig. S23 The flow chart of the information encryption and decryption operations in the Agg-CDN.



Fig. S24 Encoding states (A) A black-and-white image "SCU" (B) The absorption spectra (C) The fluorescence spectra; Encryption states (D) image units (E) The absorption spectra (F) The fluorescence spectra; Decryption states (G) A black-and-white image "SCU" (H) The absorption spectra (I) The fluorescence spectra.



Fig. S25 (A) The *MTC* absorbance spectra of 10 mM KCl and various *Lock-2* concentration. (B) The absorabnce of J-aggregates at 656nm was dissembled by various *Lock-2* concentration.

5. References

- [1] 1.F. M. Hamer, The cyanine dyes and related compounds, Interscience Publishers, New York, 1964.
- [2] G. E. Ficken, The Chemistry of Synthetic Dyes, Academic Press, New York, 1971.