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# **Supporting Information**

# Smartly designed AIE triazoliums as unique targeting fluorescence tags for sulfonic biomacromolecule recognition via 'electrostatic locking'

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#### Synthesis and characterization

*Synthesis of (2-(4-((trimethylsilyl)ethynyl)phenyl)ethene-1,1,2-triyl)tribenzene (2)* 

In a 250 mL two necked round bottom flask, 3.76 g (13.5 mmol) of 4-(2-(trimethylsilyl)ethynyl)benzophenone (1) was dissolved 100 mL dry THF under Ar. After the mixture was cooled to 0 °C, 6 mL (2.5 M in hexane, 15 mmol) of n-butyllithium was slowly added by a syringe. The mixture was stirred at 0 °C for 1 h. 3.03 g (18 mmol) of diphenylmethane was then added into the reaction mixture. The mixture was warmed to room temperature and stirred overnight. The reaction mixture was quenched upon addition of an aqueous solution of ammonium chloride and then extracted with DCM. The organic layers were collected and concentrated. The crude product and 0.17 g of p-toluenesulfonic acid were dissolved into 50 mL of toluene. The mixture was extracted with DCM. The organic layer was collected and concentrated. The crude product as purified by silica-gel chromatography using hexane as eluent to give 1 as white solid.

*Synthesis of (2-(4-ethynylphenyl) ethene-1,1,2-triyl)tribenzene (3)* 

Into a 100 mL round-bottom flask was placed THF (20 mL), 2 (643.0 mg, 1.5 mmol), and TBAF (3 mL, 1 M). After stirring for 45 min, water (60 mL) was added. The mixture was extracted with DCM ( $3 \times 20$  mL) three times and the DCM solution was washed by brine twice. The mixture was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> (5 g) for 4 h. The crude product was condensed and purified on a silica-gel column using hexane as eluent. A white solid of 6 was obtained in 95.3% yield.<sup>1</sup>

#### Synthesis of TPE-Ph $(4)^2$

Azide ethyl benzene (50 mg, 0.34 mmol) in THF (5 mL) was added to a solution of **3** (107 mg, 0.3 mmol) in THF (5 mL) with stirring. Then CuSO<sub>4</sub>· 5H<sub>2</sub>O (5.5 mg) followed by sodium ascorbate (87 mg) dissolved in water (2 mL) were added to the solution. The color of the mixture immediately turned brown and after a few minutes became dark purple. The solution was heated at about 65 °C for 24 h. The reaction mixture was diluted with H<sub>2</sub>O (5 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). After the solvent was evaporated, the crude product was purified by a silica gel column using dichloromethane/petroleum ether (1:5, v/v) as the eluent affording a white solid in a yield of 83%. <sup>1</sup>H NMR (400 MHz, DMSO-

*d*<sub>6</sub>): δ (ppm) 3.22 (t, 2H), 4.65 (t, 2H), 7.00-7.05 (m, 8H), 7.16-7.30 (m, 14H), 7.58 (d, 2H), 8.47 (s, 1H) <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ (TMS, ppm): 36.66, 51.67, 119.78, 125.01, 126.53, 127.14, 127.70, 128.71, 128.85, 131.32, 131.76, 137.71, 140.47, 143.67, 147.41. ESI (+)-MS: calcd. for C<sub>37</sub>H<sub>32</sub>N<sub>3</sub>: 503.2361 [M<sup>+</sup>]; found 504.2430 [M<sup>+</sup>+H].

Synthesis of AIETI (5a)

First **4** (0.086 g, 1.7 mmol) was dissolved in THF (5 mL) and then placed in a twoneck sealed flask fitted with an efficient reflux condenser and a balloon. Then methyl iodide (0.1 mL, 1.6 mmol) was injected into the solution. The reaction mixture was heated at 65 °C for two days. The volatiles were then removed from the resulting liquid to furnish crude product. The crude product was purified by a silica gel column using a dichloromethane– acetonitrile mixture (1:10, v/v) to afford the product as a pale yellow solid powder (yield 70%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 3.30 (t, 2H), 4.21 (s, 3H), 4.89 (t, 2H), 7.02-7.04 (m, 6H), 7.17-7.32 (m, 16H), 7.53 (d, 2H), 9.14 (s, 1H). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 34.89, 39.44, 54.54, 120.97, 127.35, 128.35, 128.52, 129.27, 130.99, 131.12, 136.71, 139.75, 142.31, 142.95, 143.13, 146.9. ESI (+)-MS: calcd. for C<sub>37</sub>H<sub>32</sub>N<sub>3</sub><sup>+</sup>: 518.2596 [M<sup>+</sup>]; found 518.2596 [M<sup>+</sup>].

### Synthesis of AIETBF (5b)

A solution of **4** (201.2 mg, 0.4 mmol) and trimethyloxonium tetrafluoroborate (296 mg, 2 mmol) in 30 mL dichloromethane was stirred under nitrogen at room temperature overnight. Water (10 mL) was then added to quench the alkylating agent. After continuous extraction with dichloromethane, the organic layer was removed in vacuo. The oily residue was then dissolved in a small amount of dichloromethane and was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/ACN = 1/2). A yellow precipitate was obtained, and then filtered and dried to get the final product. Yield 75%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) 3.30 (t, 2H), 4.22 (s, 3H), 4.89 (t, 2H), 7.00-7.04 (m, 6H), 7.15-7.34 (m, 16H), 7.52 (d, 2H), 9.13(s, 1H). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ (TMS, ppm): 34.89, 39.46, 54.56, 120.97, 127.47, 128.35, 128.53, 129.14, 129.27, 131.12, 132.02, 139.77, 142.31, 142.69, 143.11, 146.82. ESI (+)-MS: calcd. for C<sub>37</sub>H<sub>32</sub>N<sub>3</sub>: 518.26 [M<sup>+</sup>]; found 518.2596 [M<sup>+</sup>], 519.2684 [M<sup>+</sup>+H].



Fig. S2. 13C NMR spectrum of TPE-Ph in DMSO-d<sub>6</sub>



Fig. S4. <sup>1</sup>H NMR spectrum of AIETI in DMSO-*d*<sub>6</sub>



Fig. S5. <sup>13</sup>C NMR spectrum of AIETI in DMSO-d<sub>6</sub>



Fig. S6. Mass spectrum of AIETI





Fig. S9. Mass spectrum of AIETBF



Fig. S10. <sup>1</sup>H NMR spectra of AIETI (2 mM) in  $CD_3CN/D_2O$  mixture. The volume fraction of water: (a) 50%; (b) 75%; (c) 90%



Fig. S11. PL spectra of the AIETBF with SDS, NNS and PLP



Fig. S12. Effect of pH on the fluorescence intensity in 10 mM Tris-HCl buffer.



Fig. S13. Fluorescence intensity of AIETBF (40  $\mu M$ ) and Hep (1.5  $\mu g/mL)$  with time. slit 5/5.



Fig. S14. PL spectra of the AIETBF with SCD and Chs with and without PA.



Fig. S15. Fluorescence intensity of AIETBF-Hep as a function of PA concentration (40  $\mu$ M in 10mM Tris -HCl buffer solution, pH = 6.0, Hep 1.5  $\mu$ g/mL, slit 10/10).

Crystal	AIETBF		
Formula	$C_{37}H_{32}BF_4N_3$		
fw [g·mol⁻¹]	605.46		
crystal system	Monoclinic		
space group	$P2_{1}/c$		
<i>a</i> [Å]	20.354(4)		
<i>b</i> [Å]	11.829(2)		
<i>c</i> [Å]	13.889(3)		
α [°]	90.00		
β [°]	103.45(3)		
γ [°]	90.00		
V [Å <sup>3</sup> ]	3252.0(12)		
Ζ	4		

Table S1. Selected Crystallographic Data for AIETBF.

$\rho_{\rm calcd}  [{ m g/cm}^3]$	1.237
$\mu \ [\mathrm{mm}^{-1}]$	0.088
<i>T</i> [K]	113(2)
$\theta_{\min}$ - $\theta_{\max}$ [°]	2.289 - 25.017
$R/wR \ [I > 2\sigma_{(1)}]$	0.0690/ 0.1805

Table S2. Hydrogen bonds in AIETBF.

D-HA	d(D-H)	d(HA)	d(DA)	∠(DHA)
C(30)-H(30A)F(4)#1	0.99	2.56	3.303(5)	131.5
C(29)-H(29C)F(2)#2	0.98	2.41	3.066(3)	123.6
C(29)-H(29C)F(2)	0.98	2.52	3.020(4)	111.4
C(28)-H(28)F(4)#1	0.953(10)	2.54(2)	3.319(4)	139(3)
C(28)-H(28)F(3)#1	0.953(10)	2.420(19)	3.304(4)	154(3)

# **References:**

- (1) W. Z. Yuan, F. Mahtab, Y. Gong, Z.-Q. Yu, P. Lu, Y. Tang, J. W. Y. Lam, C. Zhu and B. Z. Tang, *J Mater Chem*, 2012, **22**, 10472-10479.
- (2) L. Zhang, W. Hu, L. Yu and Y. Wang, *Chem Commun*, 2015, **51**, 4298-4301.