Electronic supplementary information for the following manuscript:

**Systematic Oligoaniline-based Derivatives: the ACQ-AIE Conversion with Tunable Insertion Effect and Quantitative Fluorescence "turn-on" Detection of BSA**

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Chemicals and materials

Diphenylamine (A1, purity 98%), N,N’-diphenyl-1,4-phenylenediamine (A2, purity 98%), diphenylacetaldehyde (purity 95%), (±)-Camphor-10-sulfonic acid (purity 98%), hydroquinone (purity 99%), 4-hydroxydiphenylamine (HDPA, purity 98%), sodium tert-butoxide (purity 98%), 1,4-phenylenediamine (purity 98%), and tetrabutyl orthotitanate (TBT) were purchased from TCI (Shanghai) development Co., Ltd. N-Pheny-1,4-phenylenediamine (ADPA, purity 98%) was purchased from Alfa Aesar (China) Chemical Co., Ltd. 4-Bromodiphenylamine (Br-A1, purity 99%) was purchased from Adamas Reagent Shanghai Co., Ltd. Palladium(II) acetate (purity 99%), 2-(di-tert-butylphosphino)biphenyl, bovine serum albumin (BSA, purity 99%), cholesterol (purity 99%), carbamide (purity 99%), L-arginine (purity 99%) and glucose (purity 99%) were purchased from Innochem Chemical Reagent Beijing Co., Ltd. Phosphate buffer saline powder (2L) and γ-globulin (purity 99%) were purchased from Beijing BioDee Biotechnology Co., Ltd. 5Å molecular sieves were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd, and activated for 4 h at 240 °C in a tube furnace prior to use. Toluene and tetrahydrofuran (THF) were received from Beijing Chemical Works (Beijing, China). Toluene was dried by calcium hydride over night, then refluxed and distilled for use. All other raw materials were used without further purification.

Apparatus and analytical methods

Ultraviolet and visible (UV-vis) absorption spectra were recorded on a TU-1901 UV spectrophotometer by using THF as the solvent. Proton nuclear magnetic resonance (1H-NMR) spectra were measured on a Bruker AV 400M NMR spectrophotometer in deuterated dimethyl sulfoxide, deuterated THF or deuterated chloroform using 0.05% tetramethylsilane as an internal standard. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet iS50 FTIR spectrophotometer with KBr pellet technique at room temperature. Single crystal X-ray structures were analyzed on a Rigaku CCD Saturn 724+ X-ray single crystal diffractometer using monochromatized Mo-Kα (λ=0.71073 Å) incident radiation. Mass spectra (MS) were carried out with an Autoflex III MALDI-TOF
mass spectrometer. Photoluminescence spectra (PL) were obtained using a F-5200 fluorescence spectrophotometer. All computational studies were performed using density functional theory (DFT) method at a B3LYP/6-31G (d) level through Gaussian 09 package.\footnote{1}

**Experimental procedures**

**Synthesis of B1-A1**

A1 (0.642 g, 3.8 mmol), diphenyl acetaldehyde (0.745 g, 3.8 mmol), 5Å molecular sieves (1.011 g), toluene (8 ml) and THF (2 ml) were blended followed by mightily stirring for 20 min. Then (±)-camphor-10-sulfonic acid (catalytic amount) was added and the whole mixture refluxed at 70 °C for 8 h. Along with the system cooling to room temperature, the resulting solution was filtered and the filtrate was evaporated under reduced pressure. The crude product was dissolved in THF and recrystallized to afford bright yellow powder (0.791 g, 57%).

$^1$H-NMR (400 MHz, THF-d$_8$), $\delta$ (ppm): 5.56-5.42 (m, 5H, Ar), 5.34 (t, 4H, $J$=8.0 Hz, Ar), 5.27-5.16 (m, 9H, Ar), 5.11 (t, 2H, $J$=8.0 Hz, Ar), 4.99 (s, 1H,-N-CH=).

FTIR (KBr), cm$^{-1}$: 3021 (C-H, Ar); 1583, 1586 (C=C); 1486, 1477 (C-C, Ar); 1342, 1315, 1251 (C-N); 754, 692 (C-H, Ar).

MALDI-TOF MS: m/z: calcd for C$_{26}$H$_{21}$N: 347.2; found: 347.2(M+H)$^+$. 

**Synthesis of B1-A2, B2-A2**

B1-A2 and B2-A2 were synthesized based on the previous literature with some modifications.\footnote{2} A2 (0.880 g, 3.2 mmol), diphenyl acetaldehyde (1.393 g, 7.1 mmol) and 5Å molecular sieves (1.023 g) were added into analytical THF (2 ml) and toluene (8 ml). After stirring for 25 min, (±)-camphor-10-sulfonic acid (catalytic amount) was added. Subsequently, the solution was step-heated to 70 °C and kept reaction for 48 h. After cooling to environment temperature, filtered solvents were removed by reduced pressure distillation and the mixture was separated by silica gel column chromatography using petroleum ether/ethyl acetate (30:1 (v/v)) as the eluent. Ideal B1-A2 (Rf=0.43) and B2-A2
(Rf=0.61) were further purified by recrystallization in THF solvent. Yellow powder of B2-A2 was acquired in a yield of 53% while B1-A2 with quantity of 27% exhibiting bright yellow color was obtained.

**B1-A2:**

$^1$H-NMR (400 MHz, THF-d$_8$), $\delta$ (ppm): 9.01 (s, 1H, NH), 5.44-4.79 (m, 25H, Ar and -N-CH=).

FTIR (KBr), cm$^{-1}$: 3047 (N-H); 3022 (C-H, Ar); 1595, 1569 (C=C); 1509, 1491 (C-C, Ar); 1309, 1265 (C-N); 755, 693 (C-H, Ar).

MALDI-TOF MS: m/z: calcd for C$_{32}$H$_{26}$N$_2$: 438.2; found: 438.3 (M+H)$^+$.  

**B2-A2:**

$^1$H-NMR (400 MHz, THF-d$_8$), $\delta$ (ppm): 5.42-5.30 (m, 12H, Ar), 5.23 (t, 6H, $J$=2.0 Hz, Ar), 5.15-4.98 (m, 12H, Ar), 4.81 (s, 6H, Ar and -N-CH=).

FTIR (KBr), cm$^{-1}$: 3022 (C-H, Ar); 1591, 1569 (C=C); 1502, 1490 (C-C, Ar); 1336, 1311, 1263 (C-N); 758, 696 (C-H, Ar).

MALDI-TOF MS: m/z: calcd for C$_{36}$H$_{36}$N$_2$: 616.3; found: 616.2 (M+H)$^+$.  

**Synthesis of aniline trimer (A3)**

Aniline trimer was synthesized based on the previous literature with some modifications. $^3$ ADPA (4.500 g, 24.0 mmol) was added to a 250 ml round-bottom flask followed by dissolution with 75 ml dehydrated toluene. Afterwards, TBT (9.290 g, 80.0 mmol) was then added with a syringe all at once through the septum. The system was then vacuumed and filled with argon gas atmosphere. Repeating this operation three times to fully extirpate air, and then HDPA (4.501 g, 24.0 mmol) dissolved in 25 ml dehydrated toluene was added to the reaction system with protection of an argon gas balloon. The reaction system was step-heated to 100 °C to gain reflux condition and continued to stir for 20 hours. After allowing cooling down to room temperature, the reaction solution was filtered by sand core funnel and the resulting purple silver crystals were washed repeatedly with 700 ml of toluene. Solid crude product was purified by recrystallization
using toluene/ethyl acetate as the solvent, followed by drying under reduced pressure to obtain ideal A3 (6.307 g, 70%).

\(^1\)H-NMR (400 MHz, DMSO-d\(_6\)), \(\delta\) (ppm): 7.78 (s, 2H, NH), 7.67 (s, 1H, NH), 7.15 (t, 4H, \(J=8.0\) Hz, Ar), 7.04-6.84 (m, 12H, Ar), 6.69 (t, 2H, \(J=8.0\) Hz, Ar).

FTIR (KBr), cm\(^{-1}\): 3388 (N-H); 3044, 3020 (C-H, Ar); 1529, 1494 (C-C, Ar); 1304, 1225 (C-N); 822, 746, 694 (C-H, Ar).

MALDI-TOF MS: m/z: calcd for C\(_{24}\)H\(_{21}\)N\(_3\): 351.2; found: 351.1 (M+H)\(^{+}\).

**Synthesis of B3-A3**

Following the similar procedure as that of compound B2-A2, just replacing A2 by A3, B3-A3 was successfully obtained. Yields of yellow B3-A3 was 17%.

**B3-A3:**

\(^1\)H-NMR (400 MHz, THF-d\(_8\)), \(\delta\) (ppm): 5.44-4.99 (m, 40H, Ar), 4.91-4.80 (m, 7H, Ar and -N-CH=), 4.71 (t, 4H, \(J=8.0\) Hz, Ar).

FTIR (KBr), cm\(^{-1}\): 3023, 2923 (C-H, Ar); 1590, 1569 (C=C); 1503 (C-C, Ar); 1312, 1260 (C-N); 752, 696 (C-H, Ar).

MALDI-TOF MS: m/z: calcd for C\(_{52}\)H\(_{51}\)N\(_3\): 885.4; found: 885.2 (M+H)\(^{+}\).

**Synthesis of B2-A4**

Firstly, the enamine derivative (Br-B1-A1) was gained by the mixture of Br-A1 (1.736 g, 7.0 mmol) and diphenyl acetaldehyde (1.393 g, 7.1 mmol) following the procedure of B1-A1. The product was light gray with a yield of 79%. Next, Br-B1-A1 (2.125 g, 5.0 mmol) was added to a 50 ml round-bottom flask followed by dissolution with 15 ml dehydrated toluene. Afterwards, the mixture solution of 1,4-phenylenediamine (0.272 g, 2.5 mmol), sodium tert-butoxide (0.865 g, 9 mmol) and 2-(di-tert-butylphosphino)biphenyl (0.700 g, 1.1 mmol) in 15 ml dehydrated toluene was then added with a syringe all at once through the septum. The system was then vacuumed and filled with argon gas atmosphere. The reaction system was step-heated to 100 °C to gain reflux condition and continued to stir for 16 hours. After allowing cooling down to room temperature, the reaction solution was filtered by sand core funnel and the resulting
yellowish-green powder was washed repeatedly with 500 ml of toluene. Solid crude product was purified by recrystallization using toluene/ethyl acetate as the solvent, followed by drying under reduced pressure to obtain ideal B2-A4 (1.017 g, 42%).

$^1$H NMR (400 MHz, DMSO-$d_6$), $\delta$ (ppm): 7.26-6.90 (m, 34H, Ar and $-\text{NH}$-), 6.82 (t, 6H, $J=8.0$ Hz, Ar), 6.74 (t, 6H, $J=8.0$ Hz, Ar and $-\text{N-CH}=$).

FTIR (KBr), cm$^{-1}$: 3419 (N-H); 3027 (C-H, Ar); 1590, 1568 (C=C); 1513, 1496 (C-C, Ar); 1309, 1265 (C-N); 755, 695 (C-H, Ar).

MALDI-TOF MS: m/z: calcd for C$_{58}$H$_{46}$N$_4$: 798.4; found: 798.2 (M+H)$^+$.  

**Synthesis of B4-A4**

Following the similar procedure as that of compound A3, using new reaction ingredients as 1,4-phenylenediamine and hydroquinone, the aniline tetramer (A4) was successfully obtained. Then, as the same as the synthesis of B1-A1~B3-A3, just replacing A3 by A4, B4-A4 was successfully obtained. Yield of yellow B4-A4 was 46%.

$^1$H-NMR (400 MHz, CDCl$_3$), $\delta$ (ppm): 7.41-7.32 (m, 8H, Ar), 7.30-7.16 (m, 28H, Ar), 7.07 (d, 8H, $J=4.0$ Hz, Ar), 6.95 (t, 8H, $J=8.0$ Hz, Ar), 6.82 (d, 6H, $J=8.0$ Hz, Ar), 6.63 (d, 8H, Ar and $-\text{N-CH}=$).

FTIR (KBr), cm$^{-1}$: 3026, 2917 (C-H, Ar); 1592, 1570 (C=C); 1500 (C-C, Ar); 1301, 1258 (C-N); 755, 696 (C-H, Ar).

MALDI-TOF MS: m/z: calcd for C$_{86}$H$_{66}$N$_4$: 1154.5; found: 1154.3 (M+H)$^+$.  

![Fig. S1 MALDI-TOF mass spectra of the synthesized oligoaniline derivatives.](image-url)
**Fig. S2** $^1$H-NMR (a) and FTIR (b) spectra of B1-A1.

**Fig. S3** $^1$H-NMR (a) and FTIR (b) spectra of B1-A2.

**Fig. S4** $^1$H-NMR (a) and FTIR (b) spectra of B2-A2.
Fig. S5 $^1$H-NMR (a), MS (b) and FTIR (c) spectra of aniline trimer A3.

Fig. S6 $^1$H-NMR (a) and FTIR (b) spectra of B3-A3.
**Fig. S7** $^1$H-NMR (a) and FTIR (b) spectra of B2-A4.

**Fig. S8** $^1$H-NMR (a) and FTIR (b) spectra of B4-A4.
Fig. S9 Normalized emission spectra of B1-A1, B1-A2, B2-A2, B3-A3, B2-A4 and B4-A4 in solid powder states (excitation wavelengths: 344 nm for B1-A1, 329 nm for B1-A2, 335 nm for B2-A2, 338 nm for B2-A4, 340 nm for B3-A3 and 353 nm for B4-A4; EX slit: 2.5 nm; EM slit: 2.5 nm).

Fig. S10 Tyndall test (a) and UV absorption curves (b) of B2-A2 at various proportions of THF and water (concentrations: 10 μM).
Fig. S11 PL spectra of B1-A1 (a), B1-A2 (b), B2-A4 (c), B3-A3 (d) and B4-A4 (e) in THF-water mixtures (concentrations: 10 μM; excitation wavelengths: 344 nm for B1-A1, 329 nm for B1-A2, 338 nm for B2-A4, 340 nm for B3-A3 and 353 nm for B4-A4; EX slit: 5 nm; EM slit: 10 nm).
Fig. S12 Fluorescence-decay profiles for B1-A1, B1-A2, B2-A2, B2-A4, B3-A3 and B4-A4 (L: solution state; S: solid powder state).
**Fig. S13** Molecular orbital and energy levels of all aniline derivatives.

**Fig. S14** Geometrical structures of B1-A1, B1-A2 and B2-A2 (a: ground states; b: excited states)
**Fig. S15** (a) Emission spectra of B3-A3 solution (10 μM; excitation wavelength: 340 nm; EX slit: 5 nm; EM slit: 10 nm) in various amount of BSA, (b) The fitted linear curve of luminescence intensity changes of B3-A3 solution in response to different amounts of BSA.

**Fig. S16** Plot of $(I/I_0)-1$ concerning B1-A1 (a), B1-A2 (b) and B2-A4 (c) in response to different amounts of BSA, where $I_0$ is the luminescence intensity without the addition of BSA.
Fig. S17 (a) Fluorescence response of B2-A2 with different BSA concentrations (1.25-6.25 mg/ml) at the different time, (b) Fluorescence response of B3-A3 with different BSA concentrations (3.75-18.75 mg/ml) at the different time.

Fig. S18 Dependence of the PL intensity of B2-A2 (a) ([B2-A2]=10 μM; [component] = 0.8mg/ml) and B3-A3 (b) ([B3-A3]=10 μM; [component] = 3 mg/ml) on different mixed components of blood serum in PBS buffer. (A) BSA; (B) γ-globulin; (C) cholesterol; (D) carbamide; (E) glucose; (F) L-arginine; (G), cholesterol, glucose, carbamide, L-arginine; (H) γ-globulin, cholesterol, glucose, carbamide, L-arginine; (I) BSA, cholesterol, glucose, carbamide, L-arginine; (J) BSA, γ-globulin, cholesterol, glucose, carbamide, L-arginine.

Table S1 Spectroscopic parameters of 6 aniline derivatives. (THF, 10μM)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\lambda_{max,abs}$/nm</th>
<th>$\lambda_{em}$/nm</th>
<th>Stokes shift/cm$^{-1}$</th>
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<tbody>
<tr>
<td>B1-A1</td>
<td>312</td>
<td>408</td>
<td>7541</td>
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<tr>
<td>B1-A2</td>
<td>330</td>
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<td>B3-A3</td>
<td>342</td>
<td>464</td>
<td>7688</td>
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<td>339</td>
<td>488</td>
<td>9007</td>
</tr>
<tr>
<td>B4-A4</td>
<td>353</td>
<td>479</td>
<td>7452</td>
</tr>
</tbody>
</table>
Table S2 Fluorescent lifetimes and quantum yields of 6 aniline derivatives in THF solutions and in solid powder states

<table>
<thead>
<tr>
<th>Compounds</th>
<th>State</th>
<th>Fluorescent lifetime / ns</th>
<th>Quantum yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1-A1</td>
<td>In THF solution</td>
<td>2.51</td>
<td>0.01</td>
</tr>
<tr>
<td>B1-A2</td>
<td>In THF solution</td>
<td>1.41</td>
<td>0.02</td>
</tr>
<tr>
<td>B2-A4</td>
<td>In THF solution</td>
<td>1.14</td>
<td>0.05</td>
</tr>
<tr>
<td>B2-A2</td>
<td>In THF solution</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>B3-A3</td>
<td>In solid powder</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>B4-A4</td>
<td>In solid powder</td>
<td>0.19</td>
<td>0.22</td>
</tr>
<tr>
<td>B1-A1</td>
<td>In solid powder</td>
<td>1.41</td>
<td>0.02</td>
</tr>
<tr>
<td>B1-A2</td>
<td>In solid powder</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td>B2-A4</td>
<td>In solid powder</td>
<td>0.83</td>
<td>0.14</td>
</tr>
<tr>
<td>B2-A2</td>
<td>In solid powder</td>
<td>0.32</td>
<td>0.55</td>
</tr>
<tr>
<td>B3-A3</td>
<td>In solid powder</td>
<td>0.51</td>
<td>0.63</td>
</tr>
<tr>
<td>B4-A4</td>
<td>In solid powder</td>
<td>0.39</td>
<td>1.56</td>
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Reference