Supplementary Information

Two Aggregation induced emission (AIE)-active Reaction-Type Probes: for Real-Time Detecting and Imaging Superoxide Anions

Hengchang Ma*, Manyi Yang, Shaoxiong Zhang, Pei Yin, Tao Wang, Yuan Yang, Ziqiang Lei*, Yucheng Ma, Yanfang Qin, Zengming Yang

Key Laboratory of Polymer Materials of Gansu Province, Key Laboratory of Eco-Environment-Related Polymer Materials Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, PR China

*E-mail: mahczju@hotmail.com; Leizq@nwnu.edu.cn.
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Synthesis of 4-(diphenylamino)benzaldehyde (TPA-CHO-1).

Triphenylamine (4.91 g, 20 mmol) was dissolved in DMF (20 mL) and placed in a 100 mL flask. Phosphorous oxychloride (10 mL) was added dropwise in ice bath, and the reaction mixture was stirred for 10 min at 0 °C. And then the mixture was refluxed at 80 °C for 3 h under N₂ atmosphere. Then, reaction was quenched with cold water (300 mL) and yellow solid was precipitated. The crude product was purified over a silica gel column with mixture (ethyl acetate /petroleum ether, 1:50) as eluent to give TPA-CHO-1 as a yellow solid (yield: 85%). ¹H NMR (600 MHz, CDCl₃) δ (TMS, ppm): 9.80 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.23 – 7.08 (m, 6H), 7.01 (d, J = 8.7 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ (TMS, ppm): 190.38 (s), 153.33 (s), 146.14 (s), 131.26 (s), 129.70 (s), 129.10 (s), 126.33 (s), 125.03 (s), 119.26 (s).

Synthesis of 4,4′-(phenylazanediyl)dibenzaldehyde (TPA-CHO-2).

Triphenylamine (4.91 g, 20 mmol) was dissolved in DMF (20 mL) and placed in a 100 mL flask. Phosphorous oxychloride (20 mL) was added dropwise in ice bath, and the reaction mixture was stirred for 10 min at 0 °C. And then the mixture was refluxed at 80 °C for 3 h under N₂ atmosphere. Then, reaction was quenched with cold water (300 mL) and yellow solid was precipitated. The crude product was purified over a silica gel column with mixture (ethyl acetate /petroleum ether, 1:20) as eluent to give TPA-CHO-2 as a yellow solid (yield: 76 %). ¹H NMR (600 MHz, CDCl₃) δ (TMS, ppm): 9.88 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.23 – 7.08 (m, 6H), 7.01 (d, J = 8.7 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ (TMS, ppm): 190.46 (s), 153.33 (s), 146.14 (s), 131.26 (s), 129.70 (s), 129.10 (s), 126.33 (s), 125.03 (s), 119.26 (s).

Synthesis of 4,4′,4″-nitrilotribenzaldehyde (TPA-CHO-3).

TPA-CHO-2 (2.87 g, 10 mmol) was dissolved in DMF (10 mL) and placed in a 100 mL flask. Phosphorous oxychloride (10 mL) was added dropwise in ice bath, and the reaction mixture was stirred for 10 min at 0 °C. And then the mixture was refluxed at 80 °C for 5 h under N₂ atmosphere. Then, reaction was quenched with cold water (300 mL) and yellow solid was precipitated. The crude product was purified over a silica gel column with mixture (ethyl acetate /petroleum ether, 1:10) as eluent to give TPA-CHO-3 as a yellow solid (yield: 73%). ¹H NMR (600 MHz, CDCl₃) δ (TMS, ppm): 9.94 (s, 3H), 7.83 (d, J = 8.6 Hz, 6H), 7.24 (d, J = 8.5 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ (TMS, ppm): 190.42, 151.14, 132.58, 131.41, 124.51.
Synthesis of TPA-CHO-1, 2, 3

![Scheme S1](image)

**Scheme S1** The synthesis of TPA-CHO-1 and TPA-CHO-2

![Scheme S2](image)

**Scheme S2** The synthesis of TPA-CHO-3


**Synthesis of diethyl 4-(4-(diphenylamino)phenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (TPA-DHP-1)**

TPA-CHO-1 (2 mmol, 0.546 g), Ethyl acetoacetate (2.4 mmol 0.3 mL), NH$_3$·H$_2$O (10 mmol 0.4 mL) were dissolved in the EtOH (30 mL). And then the mixture was refluxed at 80 °C for 8 h under N$_2$ atmosphere. The reaction mixture was concentrated by rotary evaporation. Then, the TPA-DHP-1 purified by column chromatography on silica gel (300-400 mesh) with a mixture of petroleum ether and ethyl acetate as eluent (20:1 by volume), obtaining a yellow solid (0.903 g, 91% yield). $^1$H NMR (600 MHz, $d_6$-DMSO) δ (TMS, ppm): 8.75 (s, 1H), 7.21 (t, J = 7.8 Hz, 4H), 7.05 (d, J = 8.5 Hz, 2H), 6.95 (t, J = 7.4 Hz, 2H), 6.89 (d, J = 7.8 Hz, 4H), 6.83 (d, J = 8.5 Hz, 2H), 4.81 (s, 1H), 4.04-3.92 (m, 4H), 2.23 (s, 6H), 1.09 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (150 MHz, $d_6$-DMSO) δ (TMS, ppm): 167.41 (s), 147.81 (s), 145.72 (s), 145.33 (s), 143.62 (s), 129.79 (s), 128.93 (s), 124.10 (s), 123.75 (s), 122.83 (s), 102.22 (s), 59.38 (s), 18.70 (s), 14.61 (s).

**Synthesis of tetraethyl 4,4'-((phenylazanediyl)bis(4,1-phenylene))bis(2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate) (TPA-DHP-2).**

TPA-CHO-2 (2 mmol, 0.602 g), Ethyl acetoacetate (4.8 mmol 0.6 mL), NH$_3$·H$_2$O (20 mmol 1 mL) were dissolved in the EtOH (30 mL). And then the mixture was refluxed at 80 °C for 10 h under N$_2$ atmosphere. The reaction mixture was concentrated by rotary evaporation. Then, the TPA-DHP-2 purified by column chromatography on silica gel (300-400 mesh) with a
mixture of petroleum ether and ethyl acetate as eluent (10:1 by volume), obtaining a yellow solid (1.227 g, 82% yield). $^1$H NMR (600 MHz, $d_6$-DMSO) δ (TMS, ppm): 8.72 (s, 2H), 7.16 (t, $J = 7.8$ Hz, 2H), 6.99 (d, $J = 8.4$ Hz, 4H), 6.89 (t, $J = 7.3$ Hz, 1H), 6.81 (d, $J = 7.9$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 4H), 4.79 (s, 2H), 3.97 (dd, $J = 53.4$, 10.8, 7.1 Hz, 8H), 2.22 (s, 12H), 1.08 (t, $J = 7.1$ Hz, 12H). $^{13}$C NMR (150 MHz, $d_6$-DMSO) δ (TMS, ppm): 167.40 (s), 147.99 (s), 145.68 (s), 145.42 (s), 143.27 (s), 129.63 (s), 128.81 (s), 122.39 (s), 102.21 (s), 59.35 (s), 18.71 (s), 14.57 (s).

**Synthesis of hexaethyl 4,4',4''-(nitrilotris(benzene-4,1-diyl)) tris(2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate) (TPA-DHP-3)**

TPA-CHO-3 (2 mmol, 0.758 g), Ethyl acetoacetate (7.2 mmol 0.9 mL), NH$_3$·H$_2$O (20 mmol 1 mL) were dissolved in the EtOH (30 mL). And then the mixture was refluxed at 80 °C for 10 h under N$_2$ atmosphere. The reaction mixture was concentrated by rotary evaporation. Then, the TPA-DHP-3 purified by column chromatography on silica gel (300-400 mesh) with a mixture of petroleum ether and ethyl acetate as eluent (5:1 by volume), obtaining a yellow solid (1.497 g, 75% yield). $^1$H NMR (600 MHz, $d_6$-DMSO) δ (TMS, ppm): 8.78 (s, 3H), 7.61 (d, $J = 8.8$ Hz, 6H), 6.66 (d, $J = 8.7$ Hz, 6H), 4.83 (s, 3H), 3.97 (dd, $J = 46.9$, 7.1 Hz, 12H), 2.23 (s, 18H), 1.07 (t, $J = 7.1$ Hz, 18H). $^{13}$C NMR (150 MHz, $d_6$-DMSO) δ (TMS, ppm): 167.24 (s), 147.48 (s), 145.97 (s), 131.62 (s), 129.28 (s), 126.47 (s), 117.37 (s), 102.00 (s), 59.40 (s), 18.68 (s), 14.56 (s).

**Synthesis of TPA-DHP-1, 2, 3**

**Scheme S3** The synthesis of TPA-DHP-1

**Scheme S4** The synthesis of TPA-DHP-2
Synthesis and characterization of TPA-PPA-1, TPA-PPA-2, TPA-PPA-3.

Synthesis and characterization of TPA-PPA-1.

4-bromotriphenylamine (4 mmol, 1.296 g), pyridine-4-boronic acid (4.2 mmol, 0.903 g), potassium carbonate (4 mmol, 0.552 g) and tetrakis(triphenylphosphine)palladium(0) (0.2 mmol, 5% eq., 0.231 g) were dissolved in the mixture of THF (30 mL) and MeOH (30 mL). And then the mixture was refluxed at 120 °C for 48 h under N₂ atmosphere. The reaction mixture was concentrated by rotary evaporation. Then, the N,N-diphenyl-4-(pyridin-4-yl)aniline purified by column chromatography on silica gel (300-400 mesh) with a mixture of petroleum ether and ethyl acetate as eluent (10:1 by volume), obtaining a white solid (1.1 g, 83% yield). Then, the white solid (2 mmol, 0.644 g), 4-bromomethylphenylboronic acid (2 mmol, 0.426 g) and THF (50 mL), were introduced into a clean round-bottom flask with a magnetic stirrer. Subsequently, the mixture was stirred at 90 °C for 48 h. After then, the reaction mixture was precipitated from THF, and washed using diethyl ether for several times. A yellow solid powder was obtained by filtration, and dried under vacuum at room temperature overnight. TPA-PPA-1 was a yellow solid (0.890 g, 87% yield). ¹H NMR (600 MHz, d₆-DMSO) δ (TMS, ppm): 9.03 (d, J = 6.9 Hz, 2H), 8.35 (d, J = 7.0 Hz, 2H), 7.96 (d, J = 8.9 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 7.9 Hz, 2H), 7.40 (d, J = 7.9 Hz, 4H), 7.21 (t, J = 7.4 Hz, 2H), 7.17 (d, J = 7.6 Hz, 4H), 6.93 (d, J = 8.9 Hz, 2H), 5.74 (s, 2H). ¹³C NMR (150 MHz, d₆-DMSO) δ (TMS, ppm): 154.45, 151.72, 146.00, 144.69, 136.69, 135.27, 130.46, 130.13, 127.93, 126.57, 125.75, 124.66, 123.28, 119.86, 62.36.

Synthesis and characterization of TPA-PPA-2.

Bis(4-bromophenyl)amine (3 mmol, 0.978 g), iodobenzene (3.3 mmol, 0.609 g), 1,10-phenanthroline (0.9 mmol, 0.178 g), CuI (0.3 mmol, 0.057 g), and potassium hydroxide (3 mmol, 0.168 g) were introduced to a 100 mL round-bottomed flask containing 60 mL of toluene under N₂ atmosphere. The reaction mixture was rapidly heated to the reflux temperature of 120 °C for 3 h. Then, the reaction mixture was cooled to 75 °C and extracted
by 200 mL of toluene and 150 mL of deionized water, respectively. And the organic phase was decolorized by activated carbon. The adsorbents were removed by hot filtration, and the solvent was removed by rotary evaporation. The product was subjected to further purified by column chromatography on silica gel (300-400 mesh) with a mixture of petroleum ether and ethyl acetate as eluent (5:1 by volume), obtaining a white solid (0.916 g, 76% yield). Then, the white solid (2 mmol, 0.804 g) was reacted with pyridine-4-boronic acid (4.4 mmol, 0.946 g) through Suzuki reaction. Therefore, the pure product was obtained (0.630 g, 79% yield). Finally, it was reacted with 4-bromomethylphenylboronic acid through salt-forming reaction. Reaction condition was similar to Synthesis of TPA-PP. TPA-PPA-2 was an orange solid (0.721 g, 87% yield). ¹H NMR (600 MHz, d₆-DMSO) (TMS, ppm): δ 9.23 – 9.04 (m, 4H), 8.53 - 8.39 (m, 4H), 8.14 (d, J = 18.1 Hz, 4H), 8.09 (t, J = 8.8 Hz, 4H), 7.84 (t, J = 7.0 Hz, 4H), 7.49 (d, J = 8.7 Hz, 4H), 7.48-7.40 (m, 2H), 7.33 (d, J = 12.9, 5.5 Hz, 1H), 7.27 (d, J = 6.2, 4.1 Hz, 2H), 7.22 (d, J = 8.8 Hz, 4H), 5.94-5.60 (m, 4H). ¹³C NMR (150 MHz, d₆-DMSO) δ (TMS, ppm): 154.36, 150.24, 144.96, 136.61, 135.27, 130.80, 130.33, 128.97, 127.97, 127.36, 126.95, 124.11, 123.48, 121.56, 116.31, 62.59.

Synthesis and characterization of TPA-PPA-3.

Tris(4-iodophenyl)amine (2 mmol, 1.246 g), pyridine-4-boronic acid (6.3 mmol, 1.354 g), potassium carbonate (6 mmol, 0.828 g) and tetrakis(triphenylphosphine)palladium(0) (0.3 mmol, 5% eq., 0.346 g) were dissolved in the mixture of THF (30 mL) and MeOH (30 mL). And then the mixture was refluxed at 120 °C for 48 h under N₂ atmosphere. The reaction mixture was concentrated by rotary evaporation. Then, the crude product purified by column chromatography on silica gel (300-400 mesh) with a mixture of petroleum ether and ethyl acetate as eluent (1:1 by volume), obtaining a white solid (0.599 g, 63% yield). Then, the white solid (1 mmol, 0.476 g), 4-bromomethylphenylboronic acid (3 mmol, 0.629 g) and THF (50 mL), were introduced into a clean round-bottom flask with a magnetic stirrer. Subsequently, the mixture was stirred at 90 °C for 48 h. After then, the reaction mixture was precipitated from THF, and washed using diethyl ether for several times. An orange powder was obtained by filtration, and dried under vacuum at room temperature overnight. TPA-PPA-3 was an orange solid (0.953 g, 85% yield). ¹H NMR (600 MHz, d₆-DMSO) δ (TMS, ppm): 9.16 (d, J = 6.9 Hz, 6H), 8.49 (d, J = 6.9 Hz, 6H), 8.12 (d, J = 8.5 Hz, 6H), 8.12 (s, 1H), 7.83 (d, J = 7.8 Hz, 6H), 7.48 (d, J = 4.7 Hz, 6H), 7.31 (d, J = 11.6 Hz, 6H), 5.81 (d, J = 9.1 Hz, 6H). ¹³C NMR (150 MHz, d₆-DMSO) δ (TMS, ppm): 153.33, 149.90, 145.02, 136.60, 135.28, 130.46, 129.24, 127.98, 125.32, 124.53, 124.32, 62.64.
Synthesis of TPA-PPA-1, 2, 3

**Scheme S6** The synthesis of TPA-PPA-1

**Scheme S7** The synthesis of TPA-PPA-2

**Scheme S8** The synthesis of TPA-PPA-3
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (TMS, ppm): 9.80 (s, 1H), 7.67 (d, $J$ = 8.8 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.23 – 7.08 (m, 6H), 7.01 (d, $J$ = 8.7 Hz, 2H).

**Figure S1-a.** The $^1$H NMR data spectrum of TPA-CHO-1

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 190.38 (s), 153.33 (s), 146.14 (s), 131.26 (s), 129.70 (s), 129.10 (s), 126.33 (s), 125.03 (s), 119.26 (s).

**Figure S1-b.** The $^{13}$C NMR data spectrum of TPA-CHO-1
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.88 (s, 2H), 7.77 (d, $J = 8.7$ Hz, 4H), 7.39 (t, $J = 7.9$ Hz, 2H), 7.25 (t, $J = 7.4$ Hz, 1H), 7.17 (dd, $J = 7.9, 5.9$ Hz, 6H).

**Figure S2-a.** The $^1$H NMR data spectrum of TPA-CHO-2

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 190.46 (s), 151.98 (s), 145.48 (s), 131.27 (s), 130.12 (s), 127.03 (s), 126.23 (s), 122.74 (s).

**Figure S2-b.** The $^{13}$C NMR data spectrum of TPA-CHO-2
\[^1\text{H} \text{NMR}\ (600 \text{ MHz}, \text{CDCl}_3) \delta 9.94 \ (s, 3\text{H}), 7.83 \ (d, J = 8.6 \text{ Hz}, 6\text{H}), 7.24 \ (d, J = 8.5 \text{ Hz}, 6\text{H})\].

**Figure S3-a.** The \[^1\text{H} \text{NMR}\] data spectrum of TPA-CHO-3

\[^{13}\text{C} \text{NMR}\ (150 \text{ MHz}, \text{CDCl}_3), d (\text{TMS, ppm}): 190.42, 151.14, 132.58, 131.41, 124.51\]

**Figure S3-b.** The \[^{13}\text{C} \text{NMR}\] data spectrum of TPA-CHO-3
$^1$H NMR (600 MHz, $d_6$-DMSO) $\delta$ 8.75 (s, 1H), 7.21 (t, $J = 7.8$ Hz, 4H), 7.05 (d, $J = 8.5$ Hz, 2H), 6.95 (t, $J = 7.4$ Hz, 2H), 6.89 (d, $J = 7.8$ Hz, 4H), 6.83 (d, $J = 8.5$ Hz, 2H), 4.81 (s, 1H), 4.04-3.92 (m, 4H), 2.23 (s, 6H), 1.09 (t, $J = 7.1$ Hz, 6H).

Figure S4-a. The $^1$H NMR data spectrum of TPA-DHP-1

$^{13}$C NMR (150 MHz, $d_6$-DMSO) $\delta$ 167.41 (s), 147.81 (s), 145.72 (s), 145.33 (s), 143.62 (s), 129.79 (s), 128.93 (s), 124.10 (s), 123.75 (s), 122.83 (s), 102.22 (s), 59.38 (s), 18.70 (s), 14.61 (s).

Figure S4-b. The $^{13}$C NMR data spectrum of TPA-DHP-1
1H NMR (600 MHz, dmso) δ 8.72 (s, 2H), 7.16 (t, J = 7.8 Hz, 2H), 6.99 (d, J = 8.4 Hz, 4H), 6.89 (t, J = 7.3 Hz, 1H), 6.81 (d, J = 7.9 Hz, 2H), 6.73 (d, J = 8.4 Hz, 4H), 4.79 (s, 2H), 3.97 (ddd, J = 53.4, 10.8, 7.1 Hz, 8H), 2.22 (s, 12H), 1.08 (t, J = 7.1 Hz, 12H).

Figure S5-a. The 1H NMR data spectrum of TPA-DHP-2

13C NMR (150 MHz, dmso) δ 167.40 (s), 147.99 (s), 145.68 (s), 145.42 (s), 143.27 (s), 129.63 (s), 128.81 (s), 123.80 (s), 123.17 (s), 122.39 (s), 102.21 (s), 59.35 (s), 18.71 (s), 14.57 (s).

Figure S5-b. The 13C NMR data spectrum of TPA-DHP-2
$^1$H NMR (600 MHz, $d_6$-DMSO) $\delta$ 8.78 (s, 3H), 7.61 (d, $J = 8.8$ Hz, 6H), 6.66 (d, $J = 8.7$ Hz, 6H), 4.83 (s, 3H), 3.97 (dd, $J = 46.9$, 7.1 Hz, 12H), 2.23 (s, 18H), 1.07 (t, $J = 7.1$ Hz, 18H).

Figure S6-a. The $^1$H NMR data spectrum of TPA-DHP-3

$^{13}$C NMR (150 MHz, $d_6$-DMSO) $\delta$ 167.24 (s), 147.48 (s), 145.97 (s), 131.62 (s), 129.28 (s), 126.47 (s), 117.37 (s), 102.00 (s), 59.40 (s), 18.68 (s), 14.56 (s).

Figure S6-b. The $^{13}$C NMR data spectrum of TPA-DHP-3
Photophysical Property

Table 1. Photophysical Properties of TPA-CHO-1~3, TPA-DHP-1~3 and TPA-PPA-1~3.

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<th>$\lambda_{\text{ex}}$/nm</th>
<th>$\lambda_{\text{em}}$/nm</th>
<th>$\Phi_F$/%</th>
<th>Identification of $\text{O}_2^{-}$</th>
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</table>

In this table, $\lambda_{\text{ex}}$ was the maximum absorption wavelength; $\lambda_{\text{em}}$ was the maximum emission wavelength excited by each $\lambda_{\text{ex}}$; $\Phi_F$ was the absolute fluorescence quantum yield.

Figure S7 PL spectra of TPA-CHO-1~3, TPA-DHP-1~3 and TPA-PPA-1~3. Inset: The
corresponding photographs of TPA-CHO-1~3(a, b, c), TPA-DHP-1~3(d, e, f) and TPA-PPA-1~3(g, h, i) taken under illumination at 365 nm.

**AIE performance**

**Figure S8** PL spectra of TPA-DHP-1, TPA-DHP-2 and TPA-DHP-3 in Acetone and mixture of Acetone & H$_2$O, and the Plots of corresponding PL intensity and emission wavelengths versus the H$_2$O fractions. Inset shown the images in different H$_2$O fractions (0, 50%, 95%) under UV light (concentration: 20 μM).
Solvent-induced effect

Figure S9 Fluorescence spectra of TPA-DHP-1 (a), TPA-DHP-2 (b) and TPA-DHP-3 (c) at 20 μM in different solvent.
Theoretical calculations

Figure S10 HOMO-LUMO energy levels of TPA-CHO-1~3 (a, b, c), TPA-DHP-1~3(d, e, f) and TPA-PPA-1~3(g, h, i), as estimated in Gaussian 09 using the B3LYP modification with the 6-31G* basis set.
Fig. S11 molecular structures and proposed reaction mechanism for $\text{O}_2^-$ detection.
Theoretical calculations

**Figure S12** HOMO-LUMO energy levels of TPA-DHP-1(a), TPA-DHP-2(b), TPA-DHP-3(c) (left) and corresponding aromatization products (right) as estimated in Gaussian 09 using the B3LYP modification with the 6-31G* basis set.
Cyclic voltammograms

Figure S13 Cyclic voltammograms of TPA-DHP-1(a), TPA-DHP-2(b) and TPA-DHP-3(c) in N₂-saturated 0.2 M PBS (pH 7.0), at 50 mV/s.

Structural characterization

Fig. S14 (A) PL spectra of TPA-DHP-1 before the oxidization, with O₂⁻ and the oxidation product TPA-Py-1; (B) PL spectra of TPA-PPA-3 before the oxidization, with O₂⁻ and the oxidation product TPPA.

Cell viability

Figure S15 (c) Cell viabilities of HeLa cells treated with different concentrations of TPA-DHP-1 (left) and TPA-PPA-3 (right) for 96 h by MTT assay

References:
1. Jimenez, A. J.; Fagnoni, M.; Mella, M.; Albini, A. Photoinduced electron and energy transfer in

