Electronic Supplementary Information (ESI)

Enediyne as π linker in D-π-A dyes for dye-sensitized solar cells

Youfu Wang, a Luhua Dong, a Zhiwei Zheng, b Xing Li, b Rulin Xiong, a Jianli Hua*b and Aiguo Hu* a

a Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai, 200237, China.
E-mail: hagmhsn@ecust.edu.cn

b Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China.
E-mail: jlhua@ecust.edu.cn
The synthetic protocol of related compounds is shown in Figure S1. The details of synthetic process of EDY-2 are shown in the manuscript. The Sonogashira coupling reactions between aryl halide and alkyne and subsequent Knoevenagel condensation between arylaldehyde and cyanoacetic acid are similar to the processes described in the manuscript. The related NMR and mass spectra of these compounds are shown here.

Scheme S1. Synthetic protocols of three enediyne-based donor-π-acceptor type dyes with different donor positions and numbers.
N,N-dipheyl-4-((trimethylsilyl)ethynyl)aniline (1): The synthesis of 1 was following to the literature procedure.\(^{1}\) Yield 86%. \(^1\)H-NMR (DMSO-D$_6$, 400 MHz, ppm): 7.36-7.26 (m, 6H); 7.10 (t, $J$ = 7.4 Hz, 2H); 7.04 (d, $J$ = 7.7 Hz, 4H); 6.82 (d, $J$ = 8.6 Hz, 2H); 0.20 (s, 9H). \(^{13}\)C-NMR (DMSO-D$_6$, 100 MHz, ppm): 147.82; 146.36; 132.78; 129.74; 125.04; 124.10; 120.90; 114.55; 105.60; 92.79; 0.01. HR-MS (ESI): m/z calcd. for C$_{23}$H$_{24}$NSi (M+H)$^+$: 342.1600; found: 342.1669.

4-ethynyl-N,N-diphenylaniline (2): The synthesis of 2 was following to the literature procedure.\(^{1}\) Yield 90%. \(^1\)H-NMR (DMSO-D$_6$, 400 Hz, ppm): 7.33 (dd, $J$ = 9.9, 5.1 Hz, 6H); 7.10 (t, $J$ = 7.2 Hz, 2H); 7.05 (d, $J$ = 7.2 Hz, 4H); 6.86 (d, $J$ = 8.5 Hz, 2H); 4.05 (s, 1H). \(^{13}\)C-NMR (DMSO-D$_6$, 100 MHz, ppm): 147.80; 146.44; 132.87; 129.74; 124.93; 124.01; 121.24; 114.25; 83.65; 79.65. HR-MS (ESI): m/z calcd. for C$_{20}$H$_{15}$N (M)$^+$: 269.1204; found: 269.1205.

4-bromo-3-((4-(diphenylamino)phenyl)ethynyl)benzaldehyde (4): Yield 94.6%. \(^1\)H-NMR (DMSO-D$_6$, 400 Hz, ppm): 9.99 (s, 1H); 8.10 (s, 1H); 7.96 (d, $J$ = 8.1 Hz, 1H); 7.77 (d, $J$ = 8.2 Hz, 1H); 7.45 (s, 2H); 7.36 (t, $J$ = 7.1 Hz, 4H); 7.12 (m, 6H); 6.92 (d, $J$ = 7.9 Hz, 2H). \(^{13}\)C-NMR (DMSO-D$_6$, 100 MHz, ppm): 191.90; 148.39; 146.25; 135.40; 134.01; 133.49; 132.79; 130.91; 129.82; 129.28; 125.57; 125.25; 124.33; 120.83; 113.40; 95.55; 86.17. HR-MS (ESI): m/z calcd. for C$_{27}$H$_{18}$BrNO (M)$^+$: 451.0572, found: 451.0565.

3-((4-(diphenylamino)phenyl)ethynyl)-4-((trimethylsilyl)ethynyl)benzaldehyde (5a): Yield 65%. \(^1\)H-NMR (DMSO-D$_6$, 400 Hz, ppm): 10.00 (s, 1H); 8.06 (s, 1H); 7.83 (d, $J$ = 8.0 Hz, 1H); 7.72 (d, $J$ = 8.0 Hz, 1H); 7.42 (d, $J$ = 8.4 Hz, 2H); 7.37 (t, $J$ = 7.7 Hz, 4H); 7.16-7.09 (m, 6H); 6.91 (d, $J$ = 8.4 Hz, 2H); 0.24 (s, 9H). \(^{13}\)C-NMR (DMSO-D$_6$, 100 MHz, ppm): 192.11; 148.30; 146.28; 135.71; 132.89; 132.74; 129.87; 129.25; 127.95; 126.25; 125.33; 124.39; 120.74; 113.72; 102.78;
95.17; 86.21; 54.96; -0.24. HR-MS (ESI): m/z calcd. for C_{32}H_{27}NOSi (M)^+: 469.1862, found: 469.1858.

3-((4-(diphenylamino)phenyl)ethynyl)-4-ethynylbenzaldehyde (5b): Yield 92%. 
^1H-NMR (DMSO-D_6, 400 Hz, ppm): 10.01 (s, 1H); 8.07 (s, 1H); 7.85 (d, J = 8.0 Hz, 1H); 7.76 (d, J = 8.0 Hz, 1H); 7.44 (d, J = 8.6 Hz, 2H); 7.36 (t, J = 7.8 Hz, 4H); 7.16-7.09 (m, 6H); 6.92 (d, J = 8.6 Hz, 2H); 4.82 (s, 1H). ^13C-NMR (DMSO-D_6, 100 MHz, ppm): 192.09; 148.27; 146.28; 135.79; 133.17; 132.81; 132.68; 129.82; 129.02; 127.95; 126.34; 125.23; 124.30; 120.89; 113.75; 95.04; 88.49; 86.06; 81.47. HR-MS (ESI): m/z calcd. for C_{29}H_{19}NO (M)^+: 397.1467, found: 397.1460.

2-cyano-3-((4-(diphenylamino)phenyl)ethynyl)-4-ethynylphenyl)acrylic acid (EDY-1): Yield 55%. ^1H-NMR (DMSO-D_6, 400 Hz, ppm): 8.02 (s, 2H); 7.89 (d, J = 8.3 Hz, 1H); 7.68 (d, J = 8.2 Hz, 1H); 7.42 (d, J = 8.3 Hz, 2H); 7.35 (t, J = 7.6 Hz, 4H); 7.13 (t, J = 7.4 Hz, 2H); 7.10 (d, J = 7.8 Hz, 4H); 6.91 (d, J = 8.2 Hz, 2H); 4.69 (s, 1H). ^13C-NMR (DMSO-D_6, 100 MHz, ppm): 163.05; 148.56; 146.70; 133.93; 133.28; 133.13; 132.40; 130.18; 129.05; 126.47; 126.18; 125.55; 125.42; 124.63; 121.37; 118.77; 114.33; 94.43; 87.09; 86.37; 81.69. HR-MS (ESI): m/z calcd. for C_{32}H_{20}N_{2}O_{2} (M)^+: 464.1525, found: 464.1597.

3,4-bis((4-(diphenylamino)phenyl)ethynyl)benzaldehyde (8): Yield 53%. ^1H-NMR (DMSO-D_6, 400 Hz, ppm): 9.99 (s, 1H); 8.06 (s, 1H); 7.85 (d, J = 8.0 Hz, 1H); 7.74 (d, J = 8.0 Hz, 1H); 7.42 (d, J = 7.7 Hz, 4H); 7.32 (d, J = 2.5 Hz, 8H); 7.16-7.10 (m, 4H); 7.10-7.03 (m, 8H); 6.88 (d, J = 8.3 Hz, 4H). ^13C-NMR (CDCl$_3$, 100 MHz, ppm): 191.07; 148.81; 148.54; 147.17; 147.07; 134.97; 133.35; 133.02; 132.83; 132.18; 131.78; 129.60; 129.57; 127.78; 126.88; 125.40; 125.29; 124.02; 123.89; 122.10; 121.88; 115.45; 115.11; 98.50; 95.50; 87.71; 86.79. HR-MS (ESI): m/z calcd. for C_{47}H_{32}N_{2}O (M)^+: 640.2515, found: 640.2613.
3-(3,4-bis((4-(diphenylamino)phenyl)ethynyl)phenyl)-2-cyanoacrylic acid (EDY-3): Yield 64%. $^1$H-NMR (DMSO-D$_6$, 400 Hz, ppm): 8.04 (s, 1H); 8.01 (s, 1H); 7.88 (d, $J$ = 8.0 Hz, 1H); 7.65 (d, $J$ = 8.0 Hz, 1H); 7.39 (d, $J$ = 7.5, 4H); 7.30 (m, 8H); 7.11 (m, 4H); 7.04 (m, 8H); 6.87 (t, $J$ = 6.2 Hz, 4H). $^{13}$C-NMR (DMSO-D$_6$, 100 MHz, ppm): 163.64; 148.24; 148.10; 146.31; 146.24; 132.83; 132.77; 132.67; 132.63; 132.29; 131.91; 129.90; 129.79; 129.77; 128.73; 127.06; 125.44; 125.30; 125.23; 125.13; 124.32; 124.22; 121.02; 120.82; 114.00; 113.85; 96.62; 94.62; 87.46; 86.74; 67.03. HR-MS (ESI): m/z calcd. for C$_{50}$H$_{33}$N$_3$O$_2$ (M)$^+$: 707.2573, found: 707.3050.

Reference:

Figure S1. $^1$H- and $^{13}$C-NMR spectra of compound 1.
Figure S2. $^1$H- and $^{13}$C-NMR spectra of compound 2.
Figure S3. $^1$H- and $^{13}$C-NMR spectra of compound 3.
Figure S4. $^1$H- and $^{13}$C-NMR spectra of compound 4.
Figure S5. $^1$H- and $^{13}$C-NMR spectra of compound 5a.
Figure S6. $^1$H- and $^{13}$C-NMR spectra of compound 5b.
Figure S7. $^1$H- and $^{13}$C-NMR spectra of compound EDY-1.
Figure S8. $^1$H- and $^{13}$C-NMR spectra of compound 6.
Figure S9. $^1$H- and $^{13}$C-NMR spectra of compound 7a.
Figure S10. $^1$H- and $^{13}$C-NMR spectra of compound 7b.
Figure S11. $^1$H- and $^{13}$C-NMR spectra of compound EDY-2.
Figure S12. $^1$H- and $^{13}$C-NMR spectra of compound 8.
Figure S13. $^1$H- and $^{13}$C-NMR spectra of compound EDY-3.
Figure S14. MALDI-TOF Mass spectrum of compound EDY-1.

Figure S15. MALDI-TOF Mass spectrum of compound EDY-3.