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# **Supporting Information**

## Molecular engineering of D-A- $\pi$ -A sensitizers for highly efficient

# solid-state dye-sensitized solar cells

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Spiro-OMeTAD

Fig. S1 Molecular structure of HTM Spiro-OMeTAD



Fig. S2 <sup>1</sup>H NRM (CDCl<sub>3</sub>) spectrum of 2a.

Single Mass Analysis Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0 Element prediction: Off Number of isotope peaks used for i-FIT = 2 Monoisotopic Mass, Even Electron Ions 47 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass) Elements Used: C: 0-26 H: 0-90 N: 0-2 O: 0-2 S: 0-1 Br: 0-1 23-Apr-2015 21:14:56 1: TOF MS ES+ 4.71e+003 JL-HUA ECUST institute of Fine Chem HL-LX-130 31 (0.284) Cm (29:32) 503.0242 100-%-504.0290 477.1638 505.0271 517.8377 0.0 510.0 510.0 419.3124 441.3010 420.0 430.0 440.0 480.0 490.0 450.0 460.0 470.0 т 500.0 Minimum: -1.5 300.0 100.0 Maximum: 50.0 Mass Calc. Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula 501.0271 501.0272 C26 H18 N2 O2 5 Br -0.1 -0.2 18.5 26.0 0.0





Fig. S4 <sup>1</sup>H NRM (CDCl<sub>3</sub>) spectrum of 2b.

Single Mass Analysis Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0 Element prediction: Off Number of isotope peaks used for i-FIT = 2 Monoisotopic Mass, Even Electron Ions 26 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass) Elements Used: C: 0-46 H: 0-90 N: 0-2 S: 0-2 Br: 0-1 23-Apr-2015 21:18:11 1: TOF MS ES+ 6.78e+003 JL-HUA ECUST institute of Fine Chem HL-LX-131 167 (1.124) Cm (164:169) 763.2620 100-761.2607 764.2656 %-765.2642 Minimum: Maximum: -1.5 300.0 50.0 Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula Calc. Mass 761.2607 761.2599 1.1 21.5 40.5 0.0 C45 H50 N2 S2 Br 0.8









Fig. S7 HR-MS spectrum of 3a.



Fig. S8 <sup>1</sup>H NRM (CDCl<sub>3</sub>) spectrum of 3b.

Single Mass Analysis Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0 Element prediction: Off Number of isotope peaks used for i-FIT = 2 Monoisotopic Mass, Even Electron Ions 31 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass) Elements Used: C: 0-46 H: 0-70 N: 0-2 O: 0-1 S: 0-2 Br: 0-1 26-May-2015 23:45:05 1: TOF MS ES+ JL-HUA ECUST institute of Fine Chem HL-LX-402 47 (0.396) Cm (46:51) 3.32e+002 789.2553 100-7 764.4490 767.5018 777.5532 790.2535 764,5802 779.5390 781.5303 783.4877 %-765.5057 768 5055 765.5806 780.5497 782.5209 784.5127785.4487 788.2453 769.4508 771.4711 790.4030 780.0 782.0 784.0 786.0 788.0 790.0 Minimum: Maximum: -1.5 100.0 300.0 50.0 mDa PPM DBE i-FIT i-FIT (Norm) Formula Mass Calc. Mass 789.2553 789.2548 0.6 22.5 14.2 0.0 C46 H50 N2 O S2 Br 0.5







Single Mass Analysis Tolerance = 50.0 PPM\_/ DBE: min = -1.5, max = 100.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3 Monoisotopic Mass, Even Electron Ions 58 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass) Elements Used: C: 0-93 H: 0-106 N: 0-3 O: 0-7 S: 0-2 20-Mar-2016 20:55:02 1: TOF MS ES+ JL-HUA ECUST institute of Fine Chem HL-LX-409 21 (0.223) Cm (21:25) 1.48e+003 1440,7472 100-1441.7483 1439.7444 %-1442.7488 1486,7863 1455.7584 1247,0149 1456.7377 1460 1480 1439.7123 1273,7914 1325.8833 Minimum: Maximum: -1.5 300.0 50.0 Mass PPM DBE i-FIT (Norm) Formula Calc. Mass mDa i-FIT 1440.7472 1440.7472 27.2 0.0 C93 H106 N3 07 52 0.0 0.0 42.5





Fig. S12 <sup>1</sup>H NRM (CDCl<sub>3</sub>) spectrum of 5b.



**Fig. S13** <sup>1</sup>H NRM (CO(CD<sub>3</sub>)<sub>2</sub>-*d*<sub>6</sub>) spectrum of AQ309.







Fig. S15 HR-MS spectrum of AQ309.



Fig. S16 <sup>1</sup>H NRM (CDCl<sub>3</sub>) spectrum of AQ310.



Fig. S17 <sup>13</sup>C NRM (CDCl<sub>3</sub>) spectrum of AQ310.



Fig. S18 HR-MS spectrum of AQ310.

## **Stability Test:**



Fig. S19 The efficiencies of the devices after four months.