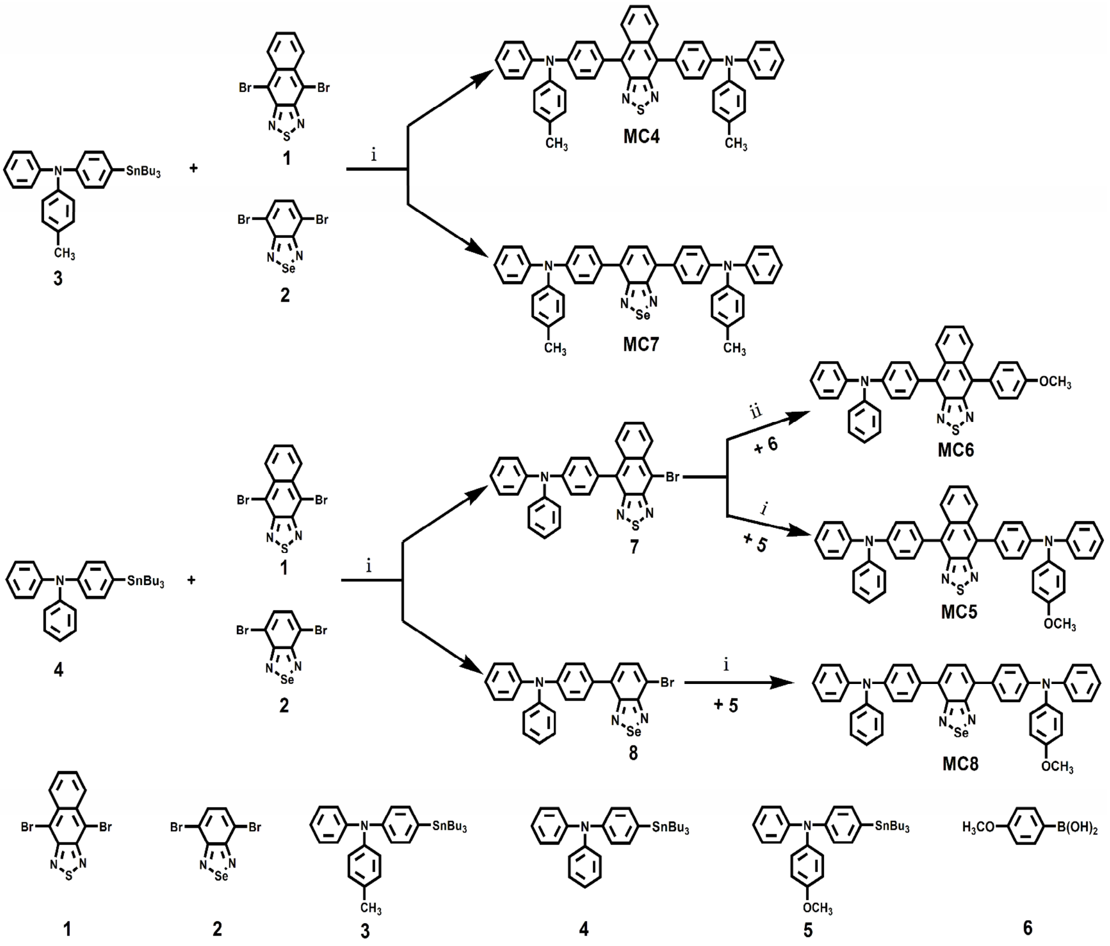
Color tuning of Novel 2,1,3-Naphthothiadiazole and 2,1,3-Benzoselenadiazole based D-A-D' Type dopants to realize highly efficient saturated red emission in non-polar solvents

Lei Chen,[ab] Lixiang Wang,*[a] Xiabin Jing[a] and Fosong Wang[a]

Supporting Information:

1. Synthesis of red MCs

All reagents were purchased from Aldrich, Acros, or Alfa and used directly without any further purification. Intermediates **1-6** were prepared as literatures [S1-S5].



Scheme S1 Syntheitic routes of red model compounds and chemical structures of intermediates (**1-5**). (Reagents and conditions: i)Pd(PPh_3)$_4$, toluene, 100 ℃; ii)Pd(PPh_3)$_4$, 2 M K_2CO_3, Aliquat 336, toluene, 90 ℃.)

*4,9-Bis(4-(*N*-phenyl-*N*-(4-methylphenyl)amino)phenyl)-*2,1,3-*naphthothiadiazole (MC4)*: A mixture of 4,9-dibromo-2,1,3-naphthothiadiazole (**1**) (0.34 g, 0.80 mmol), tributyl(4-(N-phenyl-N-(4-methylphenyl)amino)phenyl)stannane (**3**) (1.65 g, 3.0 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol) and toluene (40 mL) was heated to 100 ℃ and stirred in the dark for 24 hours. After workup, the mixture was poured to KF aqueous and stirred vigorously for 3 hours to remove the residual noxious organic stannic derivatives. After filtered, the filtrate was extracted with CH_2Cl_2, washed with brine and dried with anhydrous Na_2SO_4. The residue was purified by column chromatography (elute: petrol ether/dichloromethane 2/1) to afford a violet solid. Yield: 0.41 g (75.2%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.12 (dd, 2H), 7.53 (d, 4H), 7.35 (dd, 2H), 7.31-7.24 (m, 12H), 7.21-7.08 (m, 8H), 7.06 (t, 2H), 2.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 152.0, 148.3, 147.8, 145.2, 135.9, 134.2, 132.6, 130.5, 130.0, 129.7, 127.6, 126.2, 125.1, 123.4, 122.1, 21.3. MALDI-TOF (m/z): 700.3 [M^+].

*4,7-Bis(4-(*N*-phenyl-*N*-(4-methylphenyl)amino)phenyl)-*2,1,3-*benzoselenadiazole (MC7)*: **MC7** was synthesized following the same procedure for **MC4** using 4,7-dibromo-2,1,3-*benzoselenadiazole* (**2**) instead of 4,9-dibromo-2,1,3-naphthothiadiazole (**1**) to give a violet solid. Yield: 0.66 g (73.6%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.77 (d, 4H), 7.57 (s, 2H), 7.29-7.24 (m, 4H), 7.18-11 (m, 16H), 7.02 (t, 2H), 2.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 160.3, 148.4, 148.1, 145.3, 134.4, 133.7, 131.7, 130.5, 129.6, 128.2, 125.9, 124.8, 123.3, 122.7, 21.0. MALDI-TOF (m/z): 698.2 [M^+]

4-(4-(Diphenylamino)phenyl)-9-bromo-2,1,3-naphthothiadiazole(7): Intermediate **7** was synthesized following the similar procedure for **MC4** using tributyl(4-(diphenylamino)phenyl)stanne (**4**) instead of tributyl(4-(N-phenyl-N-(4-methylphenyl)amino)phenyl)stannane (**3**) to give a deep red solid. Yield: 0.65 g (65.3%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.49 (d, 1H), 8.15 (d, 1H), 7.61 (dd, 1H), 7.52 (d, 2H), 7.43 (dd, 1H), 7.39 (t, 4H), 7.31-7.28 (m, 6H), 7.11 (t, 2H).

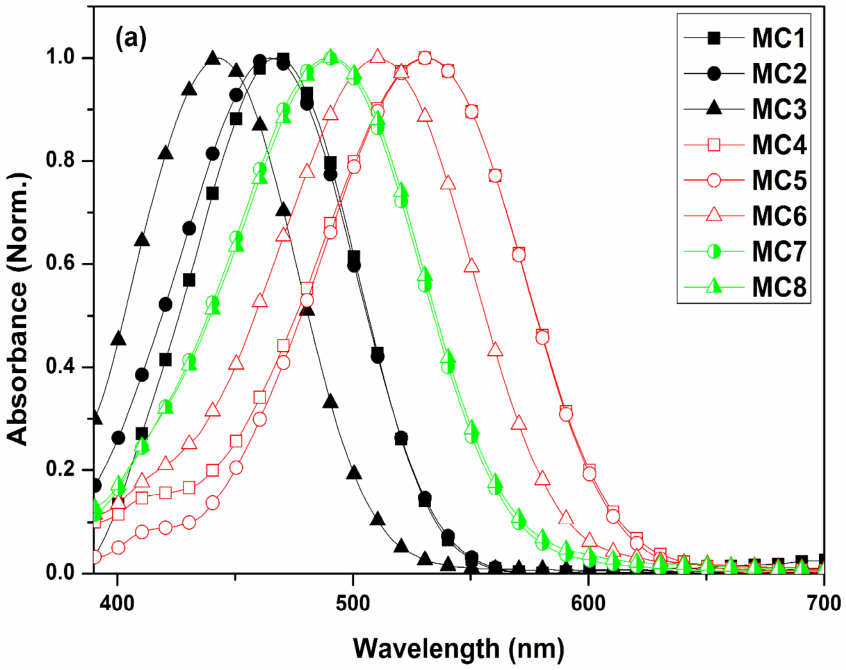
4-(4-(Diphenylamino)phenyl)-7-bromo-2,1,3-benzoselenadiazole(8): Intermediate **8** was synthesized following the similar procedure for **MC7** using tributyl(4-(diphenylamino)phenyl)stanne (**4**) instead of tributyl(4-(N-phenyl-N-(4-methylphenyl)amino)phenyl)stannane (**3**) to give a red solid. Yield: 0.47 g (87.6%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.74 (d, 1H), 7.64 (d, 2H), 7.31 (d, 1H), 7.21 (t, 4H), 7.11-7.08 (m, 6H), 6.99 (t, 2H).

4-(4-Methoxyphenyl)-7-(4-(diphenylamino)phenyl)-2,1,3-naphthothiadiazole(MC6): A mixture of 4-(4-(diphenylamino)phenyl)-9-bromo-2,1,3-naphthothiadiazole (**7**) (1.00 g, 2.00 mmol), 4-methoxyphenylboronic acid (0.46 g, 3.00 mmol), $Pd(PPh_3)_4$ (0.02 mg, 0.02 mmol), toluene (20 mL) and 2 M K_2CO_3 aqueous was kept stirred under argon in the dark at 100 ℃ for 12 h. After cooling, the solution was extracted with dichloromethane, washed with water, and then dried with anhydrous Na_2SO_4. Evaporation of solvent and purification with silica column chromatography to afford a deep red solid. Yield: 0.93 g (86.2%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.17 (dd, 1H), 8.07 (dd, 1H), 7.64 (d, 2H), 7.58 (d, 2H), 7.44-7.29 (m, 12H), 7.15 (d, 2H) ,7.11 (t, 2H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 159.9, 147.9, 132.9, 130.2, 129.8, 129.2, 127.6, 126.6, 125.6, 123.8, 122.6, 114.4, 55.79. MALDI-TOF (m/z): 535.2 [M^+].

*4-(4-(Diphenylamino)phenyl)-9-(4-(N-phenyl-N-(4-methoxy)-phenylamino)phenyl)-2,1,3-naphthothiadiazol(**MC5**)*: **MC5** was synthesized following the same procedure for **MC4** using 4-(4-(diphenylamino)phenyl)-9-bromo-2,1,3-naphthothiadiazole (**7**) and tributyl(4-(N-phenyl-N-(4-methoxy)phenylamino)phenyl)-stannane (**5**) instead of 4,9-dibromo-2,1,3-naphthothiadiazole (**1**) and tributyl(4-(N-phenyl-N-(4-methylphenyl)amino)phenyl)stannane (**3**) to give a violet solid. Yield: 0.52 g (77.3%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.05 (dd, 2H), 7.45 (t, 4H), 7.31-13 (m, 19H), 7.01-6.92 (m, 4H), 6.84 (d, 2H), 3.76(s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 157.0, 152.0, 148.2, 148.0, 132.6, 132.5, 130.3, 129.8, 129.7, 128.5, 127.6, 126.5, 125.5, 124.5, 123.8, 123.2, 122.7, 121.3, 115.4, 55.9. MALDI-TOF (m/z): 702.2 [M^+].

*4-(4-(Diphenylamino)phenyl)-7-(4-(N-phenyl-N-(4-methoxy)-phenylamino)phenyl)-2,1,3-benzoselenadiazole(**MC8**)*: **MC8** was synthesized following the same procedure for **MC4** using 4-(4-(diphenylamino)phenyl)-7-bromo-2,1,3-benzoselenadiazole(**8**) and tributyl(4-(N-phenyl-N-(4-methoxy)phenylamino)phenyl)-stannane (**5**) instead of 4,9-dibromo-2,1,3-naphthothiadiazole (**1**) and tributyl(4-(N-phenyl-N-(4-methylphenyl)amino)phenyl)stannane (**3**) to give a violet solid. Yield: 0.63 g (46.4%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.78 (t, 4H), 7.58 (s, 2H), 7.29-7.06 (m, 21H), 6.88 (d, 2H), 3.82(s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 160.3, 156.9, 148.6, 148.2, 148.0, 140.8, 134.5, 134.2, 131.3, 130.6, 129.8, 128.4, 128.2, 125.3, 124.2, 123.6, 123.3, 123.0, 122.0, 115.3, 55.9. MALDI-TOF (m/z): 700.2 [M^+].

2. Photophysical characterizations of the MCs



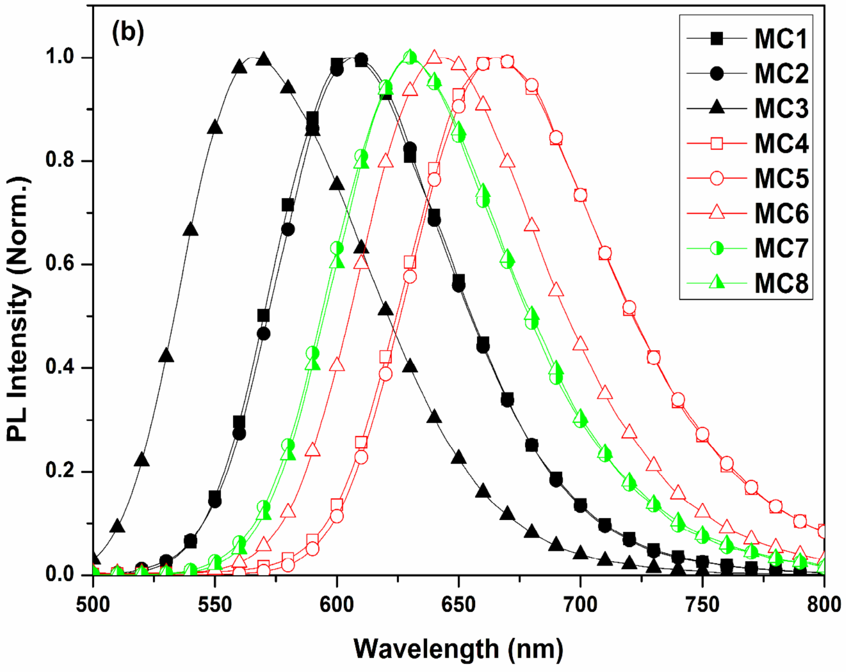


Figure S1. Absorption (a) and PL (b) spectra of red MCs in toluene solution

3. Electrochemical properties of the MCs

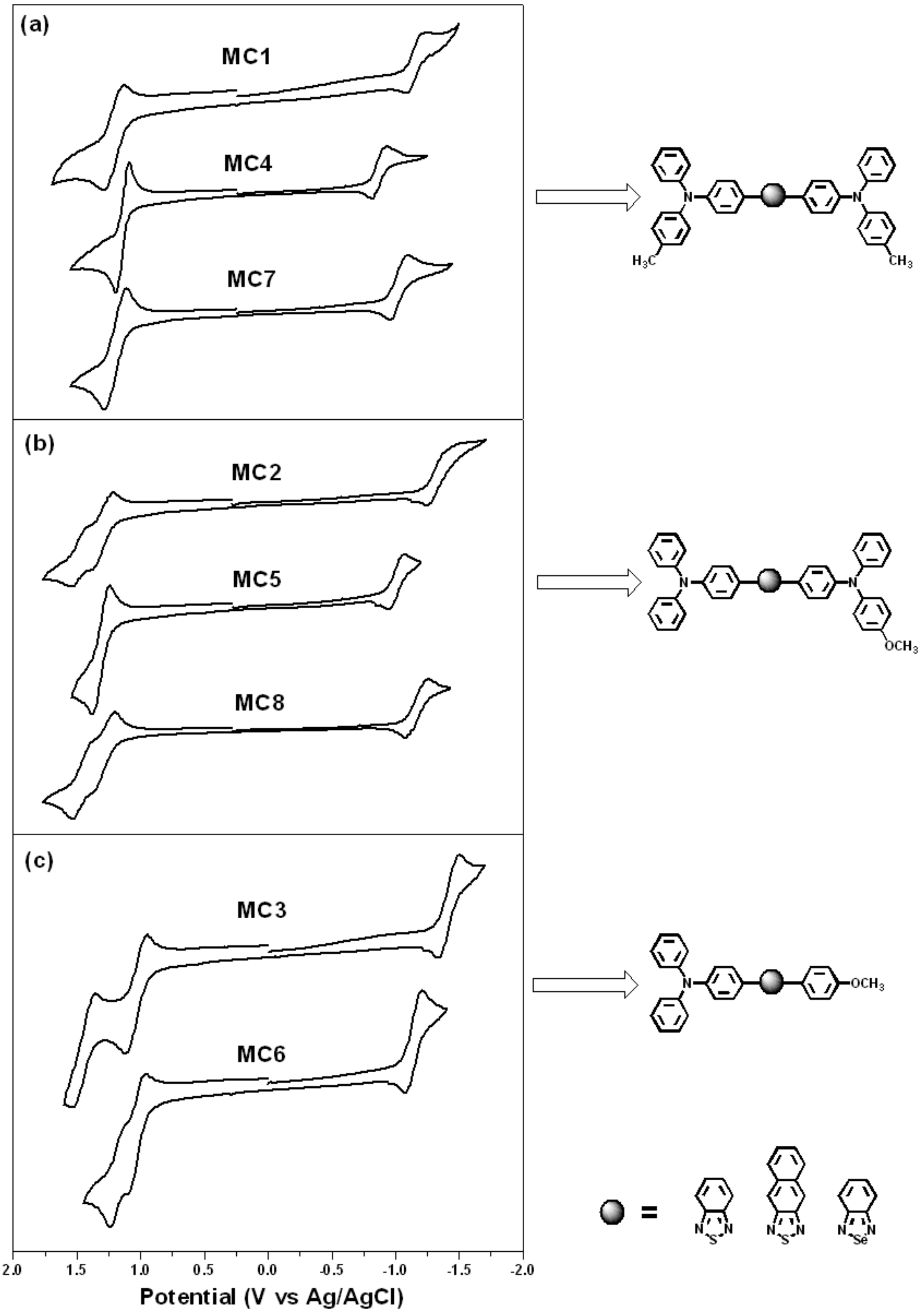


Figure S2. Cyclic voltammetry curves of the MCs

4. Experimental section

Measurement and characterization: ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AV300 NMR spectrometer. MALDI-TOF was measured by a Bruker Daltonics Flexanalysis system. UV-Vis absorption spectra were measured by a Perkin-Elmer Lambda 35 UV/Vis spectrometer. PL spectra were recorded by a Perkin-Elmer LS50B spectrofluorometer.

The relative fluorescent quantum yields of MCs in solution were calculated using the following equation[S6]: $\Phi_u = \Phi_s\,(A_s/A_u)(S_u/S_s)(n_u^2/n_s^2)$. Here, Φ is quantum yield, A is absorbance at the excitation wavelength, S is the integrated emission area across the band and n is the index of refraction of the solvent containing the unknown compound (n_u) and the standard compound (n_s). λ_{ex} is respectively 460 nm (for orange MCs) and 520 nm (for red MCs). The standard compound is Nile Red in 1,4-dioxane (0.68) for orange **MC 1-3**, and Nile Red in CH_3CN (0.78) for red **MC 4-8**.

Cyclic voltammograms of the MCs were recorded on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system at room temperature in a solution of n-Bu_4NClO_4 (0.10 M) in fresh CH_2Cl_2 at a scan rate of 100 mV/s. A Pt wire and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, a Pt disc as the working electrode respectively.

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