Electronic Supplementary Information (ESI):

O/w microemulsion: An effecticve medium for triplet-triplet annihilated upconversion with efficient triplet acceptors

Changqing Ye,[a] Bao Wang,[a,§] Xiaomei Wang,[a,*] Ping Ding,[a]

Xutang Tao,[b] Zhigang Chen,[a] Zuoqing Liang,[a] Yuyang Zhou[a]

[a]*Jiangsu Key Laboratory for Environmental Functional Materials, School of Chemistry, Biology and Materials Engineering, Suzhou University of Science and Technology, Suzhou, 215009, P. R. China.*
[b]*State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, China*

.

S1. Synthesis of triplet acceptors

2-Methyl-9,10-dinaphthylanthracene (DNAMe) Under N_2 atmosphere, *n*-butyl lithium (2.5 M, 6 mmol) was added dropwise to the solution of 2-bromonaphthalene (1.04 g, 5.04 mmol) in anhydrous THF (30 mL) at -78°C during half an hour. The mixture was stirred for another 1 hour at this temperature, then, trimethylborate (1.25 g, 12.02 mmol) was added to the mixture above at -78°C and stirred for 12 h at room temperature. The dilute HCl (2 M, 10 mL) was added and stirred for 1 h. The resulting solution was extracted with CH_2Cl_2 for three times and then the combined organic solution was dried over hydrous $MgSO_4$ overnight. The dry solution was filtered and evaporated with a rotary evaporator. The crude product was purified by column chromatography (eluent=dichloromethane/petroleum ether, 1:3 v/v) to give intermediate (naphthalenyl-2-boronic acid) with light yellow powder, yield 65.2%.

Naphthalenyl-2-boronic acid (0.43 g, 2.50 mmol), 9,10-dibromoanthracene (0.35 g, 1.01 mmol) and tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] (30 mg) were mixed in toluene (20 mL) in the presence of Na_2CO_3 (2 M, 5 mL) and ethanol (5 mL). The mixture was stirred and refluxed under the nitrogen atmosphere for 24 h. After cooling the yellow precipitate was collected by filtration and purified by column chromatography (eluent=dichloromethane/ligroin, 1:10 v/v). The product was recrystallized in toluene to get bright yellow powders, m.p. 210°C, yield 56.4%. ^{1}H NMR (DMSO, 300 MHz, ppm) δ: 2.31 (s, 3H, CH3), 7.25-7.68 (m, 13H, Ar-H), 8.04-8.19 (m, 8H, Ar-H). ^{13}C NMR (DMSO, 100 MHz, ppm) δ: 21.54, 124.400, 125.113, 125.425, 126.318, 126.410, 126.522, 127.722, 127.754, 127.894.128.000, 128.038, 128.255, 128.854, 129.021, 129.082, 129.569, 129.630, 129.661, 132.284, 132.945, 132.994, 134.751, 135.408, 135.715, 135.824, 136.302. Elemental analysis: calculated for $C_{35}H_{24}$: C, 94.56; H, 5.44%. Found: C, 94.86; H, 5.17%.

2-Chloro-9,10-dinaphthylanthracene (DNACl) Naphthalenyl-2-boronic acid (0.43 g, 2.50 mmol), 2-chloro-9,10-dibromoanthracene (0.37 g, 1.0 mmol) and tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] (30 mg) were mixed in toluene (20 mL) in the presence of Na_2CO_3 (2 M, 5 mL) and ethanol (5 mL). Then, chromophore DNACl was synthesized following the procedure similar to DNAMe. DNACl was obtained with light yellow powders (m.p. 264 °C, yield, 68.2%). ^{1}H NMR (DMSO, 300 MHz, ppm) δ: 7.41-7.71 (m, 13H, Ar-H), 8.04-8.13 (m, 8H, Ar-H). ^{13}C NMR (DMSO, 100 MHz, ppm) δ: 124.344, 126.064, 126.211, 126.355, 126.444, 126.525, 126.613, 126.660, 126.712, 127.547, 127.751, 127.806, 127.974, 128.173, 128.310, 128.815, 129.165, 129.573, 129.602, 129.759, 130.096, 130.471, 132.397, 132.935, 134.884, 135.007, 135.894, 137.163. Elemental analysis: calculated for $C_{34}H_{21}Cl$: C, 87.82; H, 4.55; Cl, 7.62%. Found: C, 87.81; H, 4.87; N, 7.56%.

9,10-Di(naphthalen-1-yl)anthracene-2-carbonitrile (DNACN) On replacing 9,10-dibromoanthracene with

9,10-dibromo-anthracene-2-carbonitrile (0.36 g, 1.0 mmol), chromophore DNACN was synthesized following the procedure similar to DNAMe. Bright yellow powders, m.p. 282 ^{o}C, yield (0.32 g, 65.3%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ: 7.49-8.15 (m, 20H, Ar-H), 8.36 (s, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 29.70, 53.41, 108.61, 119.52, 124.14, 126.29, 126.61, 126.76, 126.88, 127.26, 127.55, 127.98, 128.02, 128.11, 128.16, 128.35, 128.48, 128.56, 128.65, 128.95, 129.08, 129.98, 130.26, 130.32, 130.96, 131.91, 132.95, 133.05, 133.33, 133.39, 134.77, 134.91, 135.39, 137.76. Elemental analysis: calculated for $C_{35}H_{21}N$: C, 92.28; H, 4.65; N, 3.07%. Found: C, 992.54; H, 4.72; N, 2.74%.

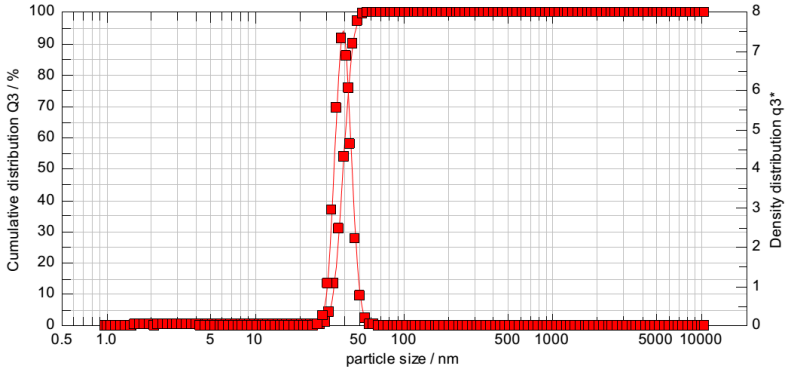

Figure S1 The nanometer size of o/w microemulsion conatining (PdMeTPP/9,10-dinaphthylanthracenes).

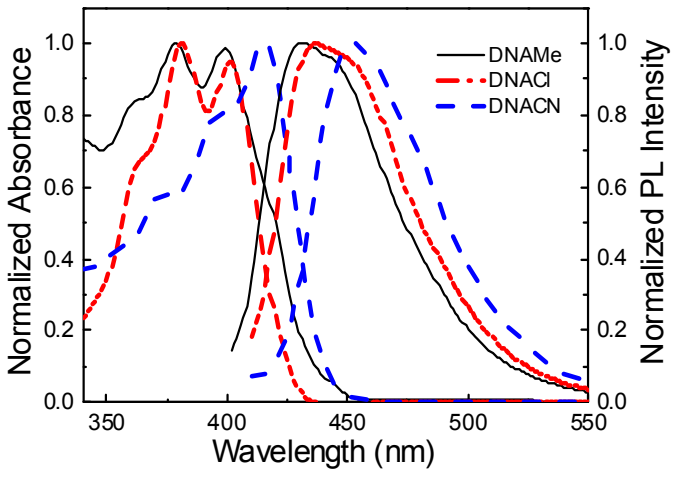

Figure S2 The absorption and emission spectra of three 9,10-dinaphthylanthracenes in o/w microemulsion medium.

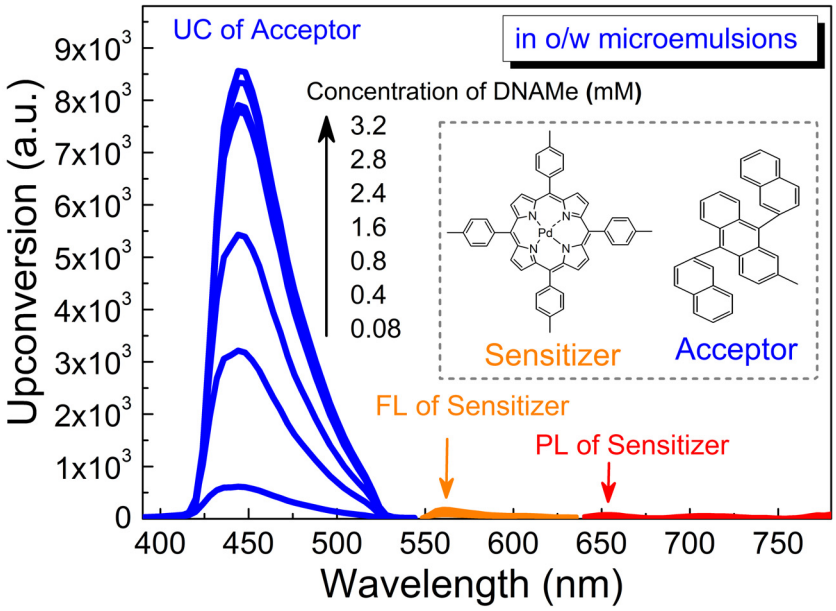

Figure S3 The concentration-dependent upconverted intensity in o/w microemulsions of DNAMe combined with sensitizer (8 μM). The excitation light source is the diode laser (532 nm, 60 mW/cm^2). The measured temperature for o/w microemulsions is at 70°C.

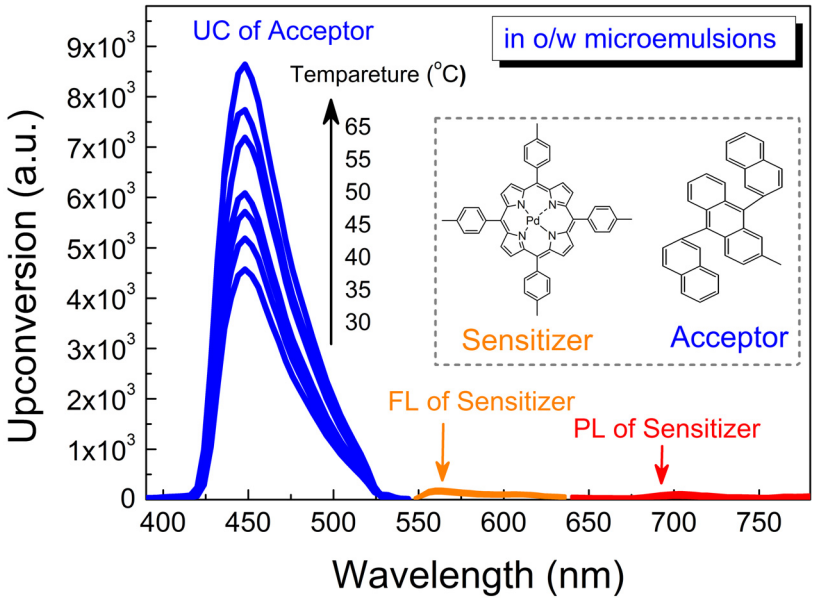

Figure S4 The temperature-dependent upconverted intensity in o/w microemulsion containing DNAMe/PdMeTPP (3.2 mM/8 μM). The excitation light source is the diode laser (532 nm, 60 mW/cm^2).

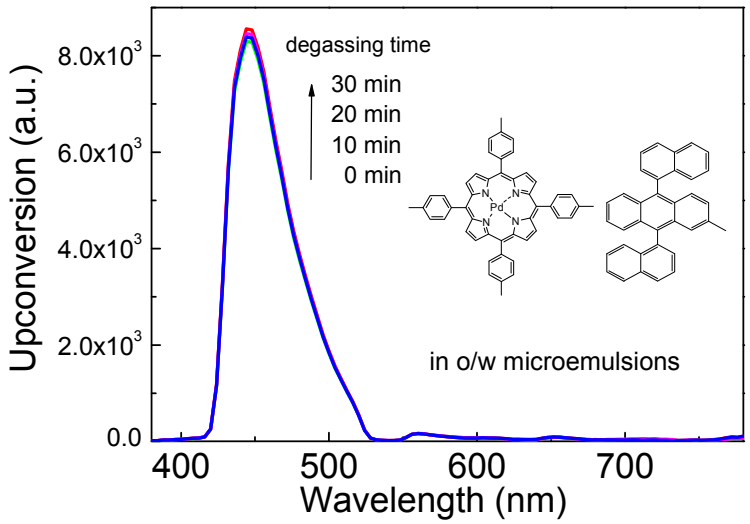

Figure S5 A comparison experiment of DNAMe/PdMeTPP (2.4 mM/8 μM) in o/w microemulsion with deaeration and without deaeration at 70°C (The excitation is diode laser at 532 nm and 60 mW/cm^2)

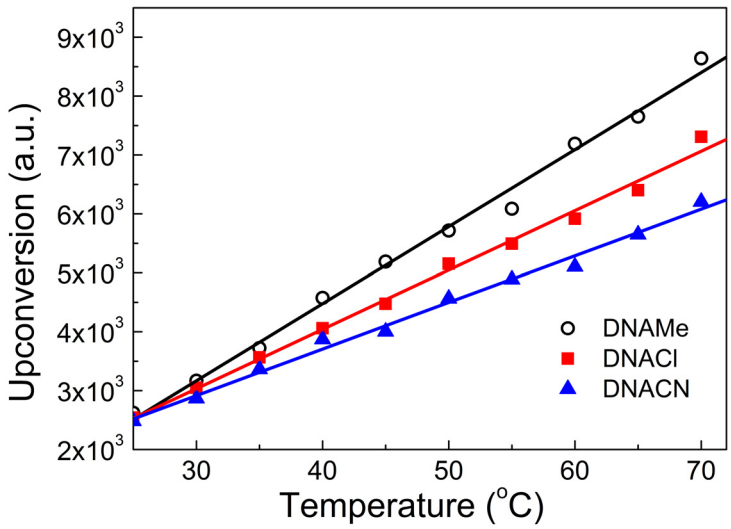

Figure S6 Temperature-dependent upconversion efficiency (Φ_{UC}) of 9,10-dinaphthylanthracenes /PdMeTPP (3.2 mM/8 μM) in o/w microemulsion without degassing (The excitation is diode laser at 532 nm and 60 mW/cm^2).

Reference

[1] Liu Y., Wang Y.F., Guo H.P., Zhu M.X., Li C., Peng J.B., Zhu W.G., and Cao Y. Synthesis and optoelectronic characterization of a monochromic red-emitting Europium(III) complex containing triphenylamine-functionalized phenanthroline. *J. Phys. Chem. C,* 115 (2011) 4209-4216.

[2] Piao X.J., Zou Y., J.C. Wu, C.Y. Li and T. Yi, Multiresponsive switchable diarylethene and its application in bioimaging. *Org. Lett.,* 11 (2009) 3818-3821.

[3] Fan C.B., Wang X. M., Ding P., Wang J. J., Liang Z.Q., Tao X. T. Synthesis, photophysical and iron-sensing properties of terpyridyl-based triphenylamine derivatives, *Dyes Pigments* 95 (2012) 757-767.

[4] Wang Z.M., Wang X.M., Zhao J.F., Jiang W.L., Yang P., Fang X.Y., Zhou M.Y., Cheng M.H. Cooperative enhancement of two-photon absorption based on electron coupling in triphenylamine-branching chromophore. *Dyes Pigments,* 79 (2008) 145-152.

[5] Ostertag, F., Weiss. J., McClements. D. J., *J. Colloid Interface Sci*., 388 (2012) 95.