Supporting information

New fluorophores based on trifluorenylamine with very large intrinsic three-photon absorption cross-sections

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Synthesis and characterization of TFA, TFA01 TFA02 and TFA03

TFA: A suspension of 1.19g **3**, 1.08g 9,9-diethyl-2-iodo-9*H*-fluorene(**4**), 30mg $Pd(OAc)_2$ and 50mg P^tBu_3 in 50ml toluene was bubbled with N_2 flush for 15 min, and then 430mg NaO^tBu was added to this suspension. The reaction mixture was heated at 100°C in dark for 23 hr. After work up the crude product was purified by chromatography (silica gel, CH_2Cl_2/hexanes =1:2) and afforded 1.49g yellow solids of **5**. (yields: 80.9%) To a suspension of 3.19g **5** in 150 ml of anhydrous DMF was added 2.30g KO^tBu, and a dark color was immediately observed inside the flask. After ~5min 3.8ml bromoethane was added and the color faded off slowly. This mixture was stirred at 45°C under N_2 atmosphere for 15hr and a pink suspension was obtained. The crude product afforded 3.16g white crystals after purification by chromatography (silica gel, CH_2Cl_2/hexanes =1:2) and recrystalization from methanol and CH_2Cl_2 (yields: 90.9%).

m.p.: 230-232°C ^{1}H NMR (500MHz, CD_2Cl_2): 7.637(d, *J* = 7.5, 3H), 7.601(d, *J* = 8.5, 3H); 7.284(m, 9H), 7.193(s, 3H), 7.088(d, *J* = 7.5, 3H), 1.967(m, 6H), 1.871(m, 6H), 0.344(t, *J* = 7.5, 18H) ^{13}C NMR (500MHz, CD_2Cl_2): 151.170, 149.665, 147.623, 141.437, 136.353, 126.822, 126.208, 122.989, 122.770, 120.166, 118.886, 118.677, 56.057, 32.634, 8.331

MALDI-TOF: m/z 677.44 [M^+] for $C_{51}H_{51}N$

Anal. Calcd. for $C_{51}H_{51}N$: C%: 90.35; H%: 7.28; N%: 2.07 Found: C%: 89.97; H%: 7.28; N%: 2.08

TFA01: A suspension of 0.80g **3**, 0.47g **11**, 20mg $Pd(OAc)_2$ and 37.5mg P^tBu_3 in 50ml toluene was bubbled with N_2 flush for 20 min until 230mg NaO^tBu was added. The reaction mixture was heated at 110°C for 17 hr. After work up the crude product was purified by chromatography (silica gel, CH_2Cl_2/hexanes =1:2) and afforded 560mg pale yellow solids. (yields: 50.2%)

m.p.: 280°C (decomposed) ^{1}H NMR (500MHz, d_6-DMSO): 7.767(m, 4H), 7.680(t, *J* = 7.5, 4H), 7.623(d, *J* = 8, 2H), 7.484(d, *J* = 7, 2H), 7.264(m, 12H), 7.074(m, 6H), 6.986(t, *J* = 6.5, 4H), 3.798(s, 4H), 1.896(m, 4H), 1.761(m, 8H), 0.289(t, *J* = 7, 6H), 0.214(t, *J* = 7, 12H) ^{13}C NMR (500MHz, $CDCl_3$): 151.116, 149.703, 147.522, 144.538, 143.046, 141.516, 136.439, 126.801, 126.222, 125.901, 124.907, 123.281, 122.729, 120.236, 119.664, 119.280, 119.003, 100.537, 56.059, 36.893, 32.725, 8.734, 8.599

MALDI-TOF: m/z 1020.5 [M^+] for $C_{77}H_{68}N_2$

Anal. Calcd. for $C_{77}H_{68}N_2$: C%: 90.55; H%: 6.71; N%: 2.74 Found: C%: 90.49; H%: 6.82; N%: 2.78

TFA02: To a yellow suspension of 0.3ml $TiCl_4$ in 15ml THF at –10°C was added 0.5g Zinc dust and the mixture was stirred for 5min at –10°C then refluxed for 5min before cooled down to 0°C. To this suspension was added a solution of 300mg **9** in 40ml THF dropwise and the reaction mixture was refluxed for 4hr. After work up the crude product was purified by chromatography (silica gel, CH_2Cl_2/hexanes=1:3) and recrystalization from CH_2Cl_2 and methanol to afford 167mg yellow solids. (yield: 57.0%)

m.p.: 280°C (decomposed) ^{1}H NMR (500MHz, $CDCl_3$): 7.618(m, 11H), 7.512(m, 4H), 7.278(m, 15H), 7.200(m, 6H), 7.093(m, 6H), 1.925(m, 24H), 0.393(t, *J* = 7.5, 9H), 0.346(t, *J* = 7.5, 27H) ^{13}C NMR (500MHz, $CDCl_3$): 151.141, 150.246, 149.687, 147.043, 141.376, 141.105, 136.440, 135.785, 128.251, 127.411, 126.839, 126.279, 125.803, 122.729, 120.421, 120.229, 119.232, 119.038, 118.724, 118.613, 56.097, 32.887, 32.769, 8.690, 8.629

MALDI-TOF: m/z 1379.9 [M^+] for $C_{104}H_{102}N_2$

Anal. Calcd. for $C_{104}H_{102}N_2$: C%: 90.52; H%: 7.45; N%: 2.03 Found: C%: 90.22; H%: 7.61; N%: 1.98

TFA03: To a suspension of 300mg **9** and 177mg **10** in 50ml THF was added 1ml KO^{t}Bu (1M) at r.t., and the reaction mixture was refluxed for 4hr until a bright yellow solution was obtained. After work up and purification by chromatography (silica gel, CH_2Cl_2/hexanes=1:3) and recrystalization from CH_2Cl_2 and methanol the crude product afforded 260mg orange solids. (yield: 75.2%)

m.p.: 300℃ (decomposed) ^{1}H NMR (500MHz, CD_2Cl_2): 7.711(d, *J* = 7.5, 2H), 7.628(m, 12H), 7.558(s, 3H), 7.529(s, 5H), 7.300(m, 16H), 7.204(s, 6H), 7.100(s, 6H), 2.120(m, 4H), 1.982(m, 14H), 1.895(m, 10H), 0.400(t, *J* = 7.5, 15H), 0.351(t, *J* = 7.5, 27H) ^{13}C NMR (500MHz, $CDCl_3$): 151.204, 150.693, 150.208, 149.677, 141.417, 140.970, 136.567, 128.642, 128.157, 126.852, 126.275, 125.805, 122.739, 120.566, 120.294, 119.861, 119.038, 56.100, 56.048, 33.001, 32.896, 32.776, 8.698, 8.634, 8.586

MALDI-TOF: m/z 1626.7 [M^+] for $C_{123}H_{120}N_2$

Anal. Calcd. for $C_{123}H_{120}N_2$: C%: 90.84; H%: 7.44; N%: 1.72 Found: C%: 91.10; H%: 7.64; N%: 1.73

Linear absorption and fluorescence spectra of TFA, TFA01, TFA02 and TFA03

UV/VIS spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer and the fluorescence spectra were measured on a Perkin-Elmer LS 50B spectrofluorimeter.

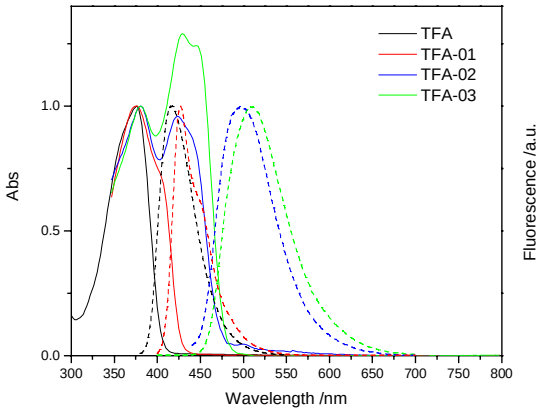

Fig. 1 Normalized linear absorption and fluorescence spectra of **TFA, TFA01, TFA02** and **TFA03** (absorption spectra: solid lines; fluorescence spectra: dash lines).