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A series of asymmetric and symmetric porphyrin derivatives: one-pot synthesis, nonlinear optical and optical limiting properties

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Fig. S1 One-pot synthesis of asymmetric and symmetric porphyrin derivatives (I-VI).

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	-695(4)	4323(2)	3291(2)	29(1)
C(2)	954(3)	3592(2)	3624(2)	23(1)
C(3)	3111(3)	3973(2)	4047(2)	26(1)
C(4)	4602(3)	3266(2)	4324(2)	25(1)
C(5)	3966(3)	2167(2)	4184(2)	22(1)
C(6)	1798(3)	1790(2)	3763(2)	26(1)
C(7)	306(3)	2496(2)	3481(2)	28(1)
C(8)	5622(3)	1417(2)	4449(2)	22(1)
C(9)	6833(3)	1527(2)	5534(2)	23(1)
C(10)	6315(4)	2210(2)	6425(2)	29(1)
C(11)	7809(4)	2131(2)	7328(2)	29(1)
C(12)	9247(3)	1400(2)	6993(2)	23(1)
C(13)	11077(3)	1145(2)	7712(2)	23(1)
C(14)	11560(4)	1648(2)	8881(2)	28(1)
C(15)	10160(4)	1447(2)	9533(2)	37(1)
C(16)	10604(5)	1950(3)	10606(2)	48(1)
C(17)	12453(5)	2642(3)	11040(2)	52(1)
C(18)	13874(5)	2843(3)	10407(2)	54(1)
C(19)	13427(4)	2347(2)	9330(2)	41(1)
C(20)	5950(3)	718(2)	3572(2)	22(1)
C(21)	4874(3)	644(2)	2450(2)	29(1)
C(22)	5789(3)	-70(2)	1855(2)	30(1)
C(23)	7475(3)	-462(2)	2584(2)	23(1)
C(24)	-1516(4)	6105(2)	3414(2)	44(1)
N(1)	8605(3)	1029(1)	5898(1)	22(1)
N(2)	7498(3)	22(1)	3620(1)	21(1)
O(1)	9(3)	5352(1)	3705(1)	37(1)
O(2)	-2469(3)	4023(2)	2728(2)	50(1)
O(3)	8660(19)	4630(5)	9177(6)	379(7)

Table S2. Bond lengths [Å] and angles [deg].

C(1)-O(2)	1.201(3)
C(1)-O(1)	1.336(3)
C(1)-C(2)	1.491(3)
C(2)-C(3)	1.386(3)
C(2)-C(7)	1.388(3)
C(3)-C(4)	1.384(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.391(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.392(3)
C(5)-C(8)	1.496(3)
C(6)-C(7)	1.385(3)
C(6)-H(6)	0.9300
C(7)-H(7)	0.9300
C(8)-C(20)	1.396(3)
C(8)-C(9)	1.408(3)
C(9)-N(1)	1.367(3)
C(9)-C(10)	1.450(3)
C(10)-C(11)	1.344(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.451(3)
C(11)-H(11)	0.9300
C(12)-N(1)	1.369(3)
C(12)-C(13)	1.407(3)
C(13)-C(23)#1	1.399(3)
C(13)-C(14)	1.493(3)
C(14)-C(19)	1.387(3)
C(14)-C(15)	1.388(3)
C(15)-C(16)	1.385(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.371(4)
C(16)-H(16)	0.9300
C(17)-C(18)	1.379(5)
C(17)-H(17)	0.9300
C(18)-C(19)	1.386(4)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-N(2)	1.378(2)
C(20)-C(21)	1.429(3)
C(21)-C(22)	1.357(3)
C(21)-H(21)	0.9300

C(22)-C(23)	1.428(3)
C(22)-H(22)	0.9300
C(23)-N(2)	1.376(3)
C(23)-C(13)#1	1.399(3)
C(24)-O(1)	1.446(3)
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
O(3)-H(3B)	0.976(9)
O(3)-H(3A)	1.054(9)

O(2)-C(1)-O(1)	123.5(2)
O(2)-C(1)-C(2)	124.1(2)
O(1)-C(1)-C(2)	112.38(19)
C(3)-C(2)-C(7)	119.42(18)
C(3)-C(2)-C(1)	121.9(2)
C(7)-C(2)-C(1)	118.65(19)
C(4)-C(3)-C(2)	120.2(2)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(3)-C(4)-C(5)	120.74(19)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(4)-C(5)-C(6)	118.79(18)
C(4)-C(5)-C(8)	119.65(18)
C(6)-C(5)-C(8)	121.53(19)
C(7)-C(6)-C(5)	120.5(2)
C(7)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
C(6)-C(7)-C(2)	120.3(2)
C(6)-C(7)-H(7)	119.8
C(2)-C(7)-H(7)	119.8
C(20)-C(8)-C(9)	125.34(18)
C(20)-C(8)-C(5)	116.46(17)
C(9)-C(8)-C(5)	117.99(18)
N(1)-C(9)-C(8)	126.18(19)
N(1)-C(9)-C(10)	111.04(18)
C(8)-C(9)-C(10)	122.78(18)
C(11)-C(10)-C(9)	106.50(19)
C(11)-C(10)-H(10)	126.8
C(9)-C(10)-H(10)	126.8
C(10)-C(11)-C(12)	106.62(19)
C(10)-C(11)-H(11)	126.7
C(12)-C(11)-H(11)	126.7

N(1)-C(12)-C(13)	125.71(18)
N(1)-C(12)-C(11)	110.82(17)
C(13)-C(12)-C(11)	123.45(19)
C(23)#1-C(13)-C(12)	125.17(19)
C(23)#1-C(13)-C(14)	116.52(18)
C(12)-C(13)-C(14)	118.31(18)
C(19)-C(14)-C(15)	118.7(2)
C(19)-C(14)-C(13)	119.8(2)
C(15)-C(14)-C(13)	121.4(2)
C(16)-C(15)-C(14)	120.5(3)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(17)-C(16)-C(15)	120.3(3)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(18)	120.0(2)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(17)-C(18)-C(19)	119.9(3)
C(17)-C(18)-H(18)	120.0
C(19)-C(18)-H(18)	120.0
C(18)-C(19)-C(14)	120.6(3)
C(18)-C(19)-H(19)	119.7
C(14)-C(19)-H(19)	119.7
N(2)-C(20)-C(8)	126.04(18)
N(2)-C(20)-C(21)	106.87(18)
C(8)-C(20)-C(21)	126.93(18)
C(22)-C(21)-C(20)	108.20(18)
C(22)-C(21)-H(21)	125.9
C(20)-C(21)-H(21)	125.9
C(21)-C(22)-C(23)	108.28(19)
C(21)-C(22)-H(22)	125.9
C(23)-C(22)-H(22)	125.9
N(2)-C(23)-C(13)#1	126.71(18)
N(2)-C(23)-C(22)	106.94(18)
C(13)#1-C(23)-C(22)	126.20(19)
O(1)-C(24)-H(24A)	109.5
O(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
O(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(9)-N(1)-C(12)	105.00(16)
C(23)-N(2)-C(20)	109.69(16)

C(1)-O(1)-C(24)	115.23(19)
H(3B)-O(3)-H(3A)	122.2(16)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1

Table S3. Anisotropic displacement parameters ($Å^2 \times 10^3$).

	U11	U22	U33	U23	U13	U12
C(1)	29(1)	32(1)	28(1)	7(1)	6(1)	14(1)
C(2)	25(1)	25(1)	19(1)	2(1)	4(1)	10(1)
C(3)	28(1)	20(1)	26(1)	0(1)	1(1)	7(1)
C(4)	20(1)	24(1)	25(1)	-2(1)	-1(1)	5(1)
C(5)	23(1)	23(1)	19(1)	3(1)	3(1)	9(1)
C(6)	24(1)	22(1)	32(1)	4(1)	4(1)	5(1)
C(7)	20(1)	30(1)	33(1)	5(1)	3(1)	5(1)
C(8)	19(1)	21(1)	24(1)	3(1)	2(1)	6(1)
C(9)	24(1)	21(1)	23(1)	2(1)	4(1)	8(1)
C(10)	31(1)	34(1)	25(1)	4(1)	7(1)	18(1)
C(11)	34(1)	32(1)	23(1)	1(1)	7(1)	15(1)
C(12)	24(1)	22(1)	22(1)	2(1)	3(1)	7(1)
C(13)	23(1)	24(1)	22(1)	0(1)	2(1)	5(1)
C(14)	30(1)	32(1)	19(1)	-1(1)	0(1)	13(1)
C(15)	37(1)	49(2)	24(1)	6(1)	4(1)	12(1)
C(16)	55(2)	67(2)	24(1)	8(1)	11(1)	24(2)
C(17)	70(2)	60(2)	20(1)	-7(1)	0(1)	24(2)
C(18)	56(2)	57(2)	36(2)	-13(1)	-4(1)	3(2)
C(19)	40(1)	46(2)	31(1)	-7(1)	5(1)	4(1)
C(20)	20(1)	21(1)	24(1)	2(1)	1(1)	6(1)
C(21)	25(1)	32(1)	25(1)	0(1)	-4(1)	12(1)
C(22)	26(1)	37(1)	22(1)	0(1)	-4(1)	12(1)
C(23)	21(1)	24(1)	21(1)	1(1)	0(1)	4(1)
C(24)	48(2)	33(1)	58(2)	16(1)	16(1)	25(1)
N(1)	22(1)	21(1)	21(1)	2(1)	2(1)	7(1)
N(2)	21(1)	20(1)	22(1)	0(1)	3(1)	6(1)
O(1)	36(1)	26(1)	48(1)	8(1)	6(1)	17(1)
O(2)	33(1)	44(1)	63(1)	7(1)	-12(1)	16(1)
O(3)	850(20)	81(4)	210(7)	-6(5)	118(12)	137(8)

Table S4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$).

	x	y	z	U(eq)
H(3)	3557	4706	4144	31
H(4)	6045	3529	4606	29
H(6)	1347	1057	3671	32
H(7)	-1137	2235	3195	33
H(10)	5173	2621	6380	35
H(11)	7903	2477	8031	35
H(15)	8913	970	9248	44
H(16)	9645	1818	11034	57
H(17)	12749	2976	11762	62
H(18)	15131	3310	10701	65
H(19)	14388	2485	8905	49
H(21)	3742	1020	2174	34
H(22)	5387	-270	1102	36
H(24A)	-877	6821	3745	66
H(24B)	-2781	5930	3667	66
H(24C)	-1904	6065	2636	66
H(3B)	7430(30)	4690(20)	8588(12)	15(6)
H(3A)	8530(40)	4640(30)	9987(12)	65(11)

Table S5. UV-Vis spectra data of six porphyrin derivatives I-VI.

Compd	Soret band, nm ($\varepsilon\times10^5$, M^{-1} cm^{-1})	Q bands, nm ($\varepsilon\times10^4$, M^{-1} cm^{-1})			
I	416 (1.83)	514 (1.67)	549 (0.81)	590 (0.5)	645 (0.52)
II	418 (1.38)	515 (0.71)	550 (0.33)	590 (0.22)	645 (0.2)
III	418 (1.8)	515 (1.38)	550 (0.66)	591 (0.43)	646 (0.35)
IV	418 (1.8)	515 (1.42)	550 (0.66)	591 (0.45)	646 (0.35)
V	419 (1.53)	516 (0.89)	550 (0.41)	590 (0.27)	646 (0.22)
VI	419 (1.23)	516 (0.68)	550 (0.31)	591 (0.21)	646 (0.16)

Table S6. Comparison of NLO coefficients with previously reported porphyrin derivatives.

Compound	Laser parameters	β (m W^{-1})	γ (m^2 W^{-1})	$\chi^{(3)}$ (esu)	F_{oL} (J cm^{-2})	ref
III	532 nm, 7 ns, 10 Hz	3.7×10^{-9}	-17×10^{-17}	17.9×10^{-11}	0.11	TW
meso-tetrakis(2,3,5,6-tetrafluoro-N,N-dimethyl-4-anilinyl)porphyrin	532 nm, 7 ns, 10 Hz	0.32×10^{-9}	-	7.9×10^{-12}	-	S1
Fluorinated trans-dicationic pyridinium porphyrin	532 nm, 7 ns, 10 Hz	75×10^{-8}	-	-	1.27	S2
Cu-porphyrin	532 nm, 6 ns, 10 Hz	132×10^{-8}	-	-	1.7	S3
Zincporphyrin	532 nm, 21 ps, 1 Hz	5.8×10^{-9}	55×10^{-17}	4.76×10^{-10}		S4
4,40-((porphyrin-5,15-diylbis(4,1-phenylene))bis(ethyne-2,1-diyl))bis(N,Ndihexadecyl aniline)	532 nm, 21 ps	6.8×10^{-12}	1.2×10^{-19}	1.60×10^{-13}	-	S5
Tetra tolyl porphyrins	532 nm, 35 ps, 10 Hz	-	-	10^{-12}	-	S6
Tetraphenyl-porphyrin film	532 nm, 30 ps, 10 Hz,	10^{-6}	10^{-13}	10^{-16}	-	S7
ZnPor-PMMA	532 nm, 21 ps, 1 Hz	4×10^{-9}	12×10^{-17}	1.64×10^{-10}		S4
ZnCu-Por-COF	532 nm, 6 ns, 10 Hz	4470×10^{-8}	-	-	-	S8
Graphene-copper porphyrin	532 nm, 6 ns, 10 Hz	4720×10^{-8}	-	8.5×10^{-12}	0.1	S8
C60/porphyrin film	532 nm, 8 ns, 1 Hz	-6.99×10^{-6}	-2.96×10^{-12}	-	-	S9

TW: This work

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