Supplementary Information

Second harmonic generation and crystal structure of self-assembled Boc-*p*-nitro-L-phenylalanyl-*p*-nitro-L-phenylalanine dipeptide

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S1 . Single-crystal X-ray diffraction crystal structure tables

Table S1.1 Atomic coordinates and U_{eq} [Å^2] for Boc-*p*NPhe*p*NPhe.

Atom	*x*	*y*	*z*	U_{eq}
O1	0.29118(15)	0.5831(3)	0.45292(10)	0.0252(4)
O2	0.37260(16)	0.8917(4)	0.38431(11)	0.0298(4)
O3	0.37792(15)	0.2247(3)	0.21525(10)	0.0259(4)
O4	0.49283(15)	0.7858(5)	0.08697(10)	0.0372(5)
O5	0.35706(16)	0.7681(6)	0.01009(11)	0.0465(7)
H5	0.404644	0.816463	−0.018434	0.070
O6	0.87785(19)	0.7354(6)	0.06213(14)	0.0575(8)
O7	0.8296(3)	0.3680(6)	0.01567(16)	0.0811(11)
O8	−0.12641(18)	0.0447(5)	0.28441(12)	0.0460(6)
O9	−0.03620(17)	0.1813(5)	0.37528(10)	0.0379(5)
N1	0.39756(17)	0.4582(4)	0.36550(11)	0.0224(5)
H1	0.384796	0.298442	0.380706	0.027
N2	0.37257(16)	0.6625(4)	0.19896(11)	0.0204(4)
H2	0.386340	0.816099	0.218140	0.024
N3	0.8283(2)	0.5295(7)	0.06325(17)	0.0485(8)
N4	−0.05570(18)	0.1776(5)	0.31124(12)	0.0280(5)
C1	0.7612(2)	0.4733(7)	0.12613(16)	0.0343(7)
C2	0.7696(2)	0.6325(6)	0.18448(16)	0.0334(7)
H2A	0.817491	0.776765	0.184830	0.040
C3	0.7065(2)	0.5782(6)	0.24312(16)	0.0289(6)
H3	0.711642	0.686578	0.284162	0.035
C4	0.6358(2)	0.3679(5)	0.24298(14)	0.0224(5)
C5	0.6300(2)	0.2087(6)	0.18293(15)	0.0290(6)
H5A	0.582304	0.063891	0.182108	0.035
C6	0.6935(3)	0.2604(6)	0.12415(16)	0.0368(7)
H6	0.690462	0.150867	0.083271	0.044
C7	0.5639(2)	0.3199(5)	0.30610(13)	0.0222(5)
H7A	0.604561	0.352917	0.350753	0.027
H7B	0.540891	0.134667	0.306182	0.027

C8	0.4646(2)	0.4977(5)	0.30378(13)	0.0196(5)
H8	0.489159	0.683792	0.303593	0.024
C9	0.40108(19)	0.4471(5)	0.23504(13)	0.0199(5)
C10	0.32030(19)	0.6543(5)	0.13007(13)	0.0212(5)
H10	0.305096	0.466103	0.119592	0.025
C11	0.3976(2)	0.7487(5)	0.07316(14)	0.0232(5)
C12	0.2116(2)	0.7964(5)	0.12995(14)	0.0230(5)
H12A	0.220658	0.977401	0.147748	0.028
H12B	0.182145	0.804591	0.080809	0.028
C13	0.1360(2)	0.6480(5)	0.17747(14)	0.0222(5)
C14	0.0719(2)	0.4507(6)	0.14841(14)	0.0233(5)
H14	0.072250	0.421599	0.098378	0.028
C15	0.0076(2)	0.2960(5)	0.19155(14)	0.0246(6)
H15	−0.036594	0.162922	0.171700	0.030
C16	0.0100(2)	0.3422(5)	0.26448(14)	0.0230(5)
C17	0.0717(2)	0.5360(5)	0.29483(15)	0.0273(6)
H17	0.071649	0.562887	0.344964	0.033
C18	0.1338(2)	0.6912(5)	0.25097(14)	0.0263(6)
H18	0.175401	0.828491	0.271122	0.032
C19	0.3544(2)	0.6646(5)	0.39997(13)	0.0224(5)
C20	0.2418(2)	0.7751(5)	0.50235(13)	0.0244(6)
C21	0.1658(2)	0.9539(6)	0.46193(15)	0.0293(6)
H21A	0.207106	1.075033	0.432419	0.044
H21B	0.122692	1.053376	0.495894	0.044
H21C	0.118581	0.848750	0.431349	0.044
C22	0.3291(2)	0.9193(6)	0.54284(16)	0.0312(6)
H22A	0.381301	0.793266	0.561588	0.047
H22B	0.297403	1.016526	0.582465	0.047
H22C	0.365052	1.041553	0.510674	0.047
C23	0.1790(3)	0.6009(6)	0.55246(16)	0.0322(7)
H23A	0.123051	0.508757	0.525533	0.048
H23B	0.146074	0.708331	0.589592	0.048
H23C	0.227462	0.473278	0.574631	0.048

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S1.2 Anisotropic displacement parameters [Å^2] for Boc-*p*NPhe*p*NPhe. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0342(10)	0.0143(9)	0.0273(10)	−0.0018(7)	0.0095(8)	−0.0004(7)
O2	0.0384(11)	0.0162(9)	0.0350(11)	0.0006(8)	0.0112(8)	−0.0010(8)
O3	0.0319(10)	0.0152(9)	0.0306(10)	0.0000(7)	−0.0049(8)	−0.0018(7)
O4	0.0224(10)	0.0580(15)	0.0314(10)	−0.0118(10)	0.0057(8)	−0.0088(10)
O5	0.0241(10)	0.087(2)	0.0285(11)	0.0211(12)	0.0049(8)	0.0037(11)
O6	0.0358(12)	0.083(2)	0.0543(15)	0.0355(15)	0.0094(11)	−0.0002(14)
O7	0.127(3)	0.0598(19)	0.0574(17)	0.0133(15)	0.0561(18)	0.0343(19)
O8	0.0393(12)	0.0543(15)	0.0446(13)	0.0103(11)	0.0003(10)	−0.0248(11)
O9	0.0444(12)	0.0422(13)	0.0271(11)	0.0060(9)	0.0083(9)	−0.0003(11)
N1	0.0304(12)	0.0134(10)	0.0235(11)	0.0017(9)	0.0054(9)	−0.0006(9)
N2	0.0238(11)	0.0142(10)	0.0232(11)	−0.0004(8)	0.0007(8)	−0.0002(8)
N3	0.0429(17)	0.059(2)	0.0443(17)	0.0198(15)	0.0162(13)	0.0248(15)

N4	0.0253(12)	0.0272(12)	0.0316(13)	0.0038(10)	0.0065(9)	0.0042(10)
C1	0.0300(15)	0.0387(17)	0.0343(15)	0.0122(14)	0.0113(12)	0.0133(13)
C2	0.0268(14)	0.0316(16)	0.0419(17)	0.0100(13)	0.0048(12)	0.0008(12)
C3	0.0258(14)	0.0296(15)	0.0313(15)	0.0026(12)	0.0013(11)	0.0001(11)
C4	0.0196(12)	0.0202(13)	0.0272(13)	0.0029(10)	−0.0006(10)	0.0050(10)
C5	0.0314(14)	0.0255(14)	0.0301(14)	−0.0019(11)	0.0026(11)	0.0029(12)
C6	0.0434(17)	0.0386(18)	0.0285(14)	−0.0038(13)	0.0050(12)	0.0130(14)
C7	0.0260(13)	0.0186(12)	0.0222(12)	0.0024(10)	0.0002(10)	−0.0005(10)
C8	0.0234(12)	0.0146(12)	0.0209(12)	0.0009(9)	0.0020(10)	−0.0005(9)
C9	0.0186(12)	0.0177(12)	0.0234(12)	−0.0002(10)	0.0062(10)	0.0014(10)
C10	0.0209(12)	0.0189(12)	0.0238(13)	0.0011(10)	−0.0008(10)	−0.0013(10)
C11	0.0229(13)	0.0214(13)	0.0254(13)	−0.0002(10)	0.0011(10)	0.0015(10)
C12	0.0235(13)	0.0187(13)	0.0268(13)	0.0032(10)	0.0005(10)	0.0012(10)
C13	0.0198(12)	0.0210(13)	0.0260(13)	0.0021(11)	0.0020(10)	0.0032(10)
C14	0.0212(12)	0.0263(13)	0.0225(13)	−0.0012(11)	0.0027(10)	0.0014(11)
C15	0.0201(12)	0.0254(14)	0.0285(14)	−0.0002(11)	−0.0005(10)	−0.0021(11)
C16	0.0201(12)	0.0231(13)	0.0260(13)	0.0027(11)	0.0056(10)	0.0025(10)
C17	0.0313(14)	0.0279(14)	0.0227(13)	−0.0028(11)	0.0052(11)	−0.0006(12)
C18	0.0273(14)	0.0217(13)	0.0298(14)	−0.0052(11)	0.0011(11)	−0.0023(11)
C19	0.0258(13)	0.0184(12)	0.0231(13)	−0.0001(10)	0.0015(10)	−0.0004(10)
C20	0.0312(14)	0.0187(13)	0.0234(13)	−0.0045(10)	0.0065(11)	0.0027(11)
C21	0.0321(14)	0.0247(13)	0.0311(14)	−0.0064(12)	0.0017(11)	0.0032(12)
C22	0.0359(15)	0.0257(15)	0.0318(15)	−0.0059(12)	−0.0010(12)	0.0014(12)
C23	0.0428(17)	0.0230(14)	0.0311(14)	−0.0038(11)	0.0127(13)	0.0003(12)

Table S1.3. Bond lengths and angles for Boc-*p*NPhe*p*NPhe.

Atom–Atom	**Length [Å]**
O1–C19	1.340(3)
O1–C20	1.487(3)
O2–C19	1.219(3)
O3–C9	1.230(3)
O4–C11	1.230(3)
O5–H5	0.8400
O5–C11	1.286(3)
O6–N3	1.222(4)
O7–N3	1.216(5)
O8–N4	1.220(3)
O9–N4	1.224(3)
N1–H1	0.8800
N1–C8	1.448(3)
N1–C19	1.352(3)
N2–H2	0.8800
N2–C9	1.339(3)
N2–C10	1.443(3)
N3–C1	1.481(4)
N4–C16	1.470(3)
C1–C2	1.367(5)
C1–C6	1.378(5)
C2–H2A	0.9500

C2–C3	1.386(4)
C3–H3	0.9500
C3–C4	1.391(4)
C4–C5	1.391(4)
C4–C7	1.511(3)
C5–H5A	0.9500
C5–C6	1.389(4)
C6–H6	0.9500
C7–H7A	0.9900
C7–H7B	0.9900
C7–C8	1.538(3)
C8–H8	1.0000
C8–C9	1.530(3)
C10–H10	1.0000
C10–C11	1.523(4)
C10–C12	1.540(3)
C12–H12A	0.9900
C12–H12B	0.9900
C12–C13	1.508(3)
C13–C14	1.395(4)
C13–C18	1.396(4)
C14–H14	0.9500
C14–C15	1.392(4)
C15–H15	0.9500
C15–C16	1.388(4)
C16–C17	1.375(4)
C17–H17	0.9500
C17–C18	1.385(4)
C18–H18	0.9500
C20–C21	1.516(4)
C20–C22	1.515(4)
C20–C23	1.518(4)
C21–H21A	0.9800
C21–H21B	0.9800
C21–H21C	0.9800
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800

Atom–Atom–Atom	Angle [°]
C19–O1–C20	120.4(2)
C11–O5–H5	109.5
C8–N1–H1	119.7
C19–N1–H1	119.7
C19–N1–C8	120.6(2)
C9–N2–H2	118.5
C9–N2–C10	123.0(2)
C10–N2–H2	118.5
O6–N3–C1	118.1(3)
O7–N3–O6	124.3(3)
O7–N3–C1	117.6(3)
O8–N4–O9	123.5(2)
O8–N4–C16	118.6(2)
O9–N4–C16	118.0(2)
C2–C1–N3	118.8(3)
C2–C1–C6	122.3(3)
C6–C1–N3	118.9(3)
C1–C2–H2A	120.8
C1–C2–C3	118.4(3)
C3–C2–H2A	120.8
C2–C3–H3	119.4
C2–C3–C4	121.2(3)
C4–C3–H3	119.4
C3–C4–C7	120.3(2)
C5–C4–C3	118.9(2)
C5–C4–C7	120.8(2)
C4–C5–H5A	119.9
C6–C5–C4	120.3(3)
C6–C5–H5A	119.9
C1–C6–C5	118.9(3)
C1–C6–H6	120.5
C5–C6–H6	120.5
C4–C7–H7A	109.3
C4–C7–H7B	109.3
C4–C7–C8	111.5(2)
H7A–C7–H7B	108.0
C8–C7–H7A	109.3
C8–C7–H7B	109.3
N1–C8–C7	111.5(2)
N1–C8–H8	108.4
N1–C8–C9	110.5(2)
C7–C8–H8	108.4
C9–C8–C7	109.7(2)
C9–C8–H8	108.4
O3–C9–N2	123.2(2)
O3–C9–C8	122.0(2)
N2–C9–C8	114.9(2)
N2–C10–H10	106.7
N2–C10–C11	109.5(2)
N2–C10–C12	112.3(2)
C11–C10–H10	106.7
C11–C10–C12	114.4(2)

C12–C10–H10	106.7
O4–C11–O5	123.6(2)
O4–C11–C10	121.2(2)
O5–C11–C10	115.0(2)
C10–C12–H12A	110.0
C10–C12–H12B	110.0
H12A–C12–H12B	108.4
C13–C12–C10	108.5(2)
C13–C12–H12A	110.0
C13–C12–H12B	110.0
C14–C13–C12	119.5(2)
C14–C13–C18	118.9(2)
C18–C13–C12	121.4(2)
C13–C14–H14	119.5
C15–C14–C13	121.1(2)
C15–C14–H14	119.5
C14–C15–H15	121.0
C16–C15–C14	117.9(2)
C16–C15–H15	121.0
C15–C16–N4	118.9(2)
C17–C16–N4	118.6(2)
C17–C16–C15	122.5(2)
C16–C17–H17	120.6
C16–C17–C18	118.8(2)
C18–C17–H17	120.6
C13–C18–H18	119.6
C17–C18–C13	120.7(2)
C17–C18–H18	119.6
O1–C19–N1	110.5(2)
O2–C19–O1	125.9(2)
O2–C19–N1	123.6(2)
O1–C20–C21	110.3(2)
O1–C20–C22	109.5(2)
O1–C20–C23	102.6(2)
C21–C20–C23	109.8(2)
C22–C20–C21	113.7(2)
C22–C20–C23	110.4(2)
C20–C21–H21A	109.5
C20–C21–H21B	109.5
C20–C21–H21C	109.5
H21A–C21–H21B	109.5
H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
C20–C22–H22A	109.5
C20–C22–H22B	109.5
C20–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
C20–C23–H23A	109.5
C20–C23–H23B	109.5
C20–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5

Table S1.4. Torsion angles for Boc-*p*NPhe*p*NPhe.

Atom–Atom–Atom–Atom	Torsion Angle [°]
O6–N3–C1–C2	−9.7(4)
O6–N3–C1–C6	171.2(3)
O7–N3–C1–C2	171.0(3)
O7–N3–C1–C6	−8.1(4)
O8–N4–C16–C15	−15.3(4)
O8–N4–C16–C17	164.9(3)
O9–N4–C16–C15	164.6(2)
O9–N4–C16–C17	−15.2(4)
N1–C8–C9–O3	−74.7(3)
N1–C8–C9–N2	104.9(2)
N2–C10–C11–O4	9.4(4)
N2–C10–C11–O5	−175.1(2)
N2–C10–C12–C13	−66.2(3)
N3–C1–C2–C3	−179.9(3)
N3–C1–C6–C5	−179.5(3)
N4–C16–C17–C18	179.9(2)
C1–C2–C3–C4	−0.3(4)
C2–C1–C6–C5	1.4(4)
C2–C3–C4–C5	0.8(4)
C2–C3–C4–C7	−177.1(2)
C3–C4–C5–C6	−0.3(4)
C3–C4–C7–C8	80.7(3)
C4–C5–C6–C1	−0.8(4)
C4–C7–C8–N1	−178.0(2)
C4–C7–C8–C9	59.2(3)
C5–C4–C7–C8	−97.1(3)
C6–C1–C2–C3	−0.9(4)
C7–C4–C5–C6	177.6(3)
C7–C8–C9–O3	48.6(3)
C7–C8–C9–N2	−131.8(2)
C8–N1–C19–O1	176.8(2)
C8–N1–C19–O2	−3.7(4)
C9–N2–C10–C11	−109.6(3)
C9–N2–C10–C12	122.1(2)
C10–N2–C9–O3	−5.8(4)
C10–N2–C9–C8	174.7(2)
C10–C12–C13–C14	−90.4(3)
C10–C12–C13–C18	85.2(3)
C11–C10–C12–C13	168.2(2)
C12–C10–C11–O4	136.5(3)
C12–C10–C11–O5	−48.0(3)
C12–C13–C14–C15	174.9(2)
C12–C13–C18–C17	−173.6(2)
C13–C14–C15–C16	−0.7(4)
C14–C13–C18–C17	1.9(4)
C14–C15–C16–N4	−178.8(2)
C14–C15–C16–C17	1.1(4)
C15–C16–C17–C18	0.0(4)
C16–C17–C18–C13	−1.6(4)
C18–C13–C14–C15	−0.8(4)
C19–O1–C20–C21	63.3(3)
C19–O1–C20–C22	−62.5(3)

C19–N1–C8–C7	137.0(2)
C19–N1–C8–C9	−100.8(3)
C20–O1–C19–O2	−4.5(4)
C20–O1–C19–N1	174.9(2)
C19–O1–C20–C23	−179.8(2)

S2. Estimating the effective second-order nonlinear susceptibility

To estimate the effective second-order nonlinear susceptibility, d_{eff}, of the Boc-*p*NPhe*p*NPhe crystals we calibrated the efficiency of our second harmonic generation microscope using the second harmonic signal generated from a 1 mm thick orientated beta barium borate (BBO) crystal.

Accounting for both spatial walk-off and temporal dephasing from group velocity mismatch, Wang and Weiner [1] estimated the efficiency of generating second harmonic light using ultra-short pulses as:

$$\epsilon = \frac{U_{2\omega}}{U_{\omega}} = \frac{4\omega^2 d_{eff}^2}{n_{\omega} n_{2\omega} \lambda_0 \varepsilon_0 c^3} \sqrt{2\,ln\,2}\, \frac{U_{\omega}}{t_p}\, \ell_{st}\, tan^{-1}\left(\frac{L}{2z_R}\right) \qquad \text{(S.1)}$$

Here U_{ω} and $U_{2\omega}$ are the fundamental and second harmonic pulse energies, respectively, t_p is the incident laser's pulse full width at half-maximum duration assuming a Gaussian temporal profile. The refractive indices at the fundamental and second harmonic frequencies are n_{ω} and $n_{2\omega}$, while L is the crystal thickness and z_R is the focused laser's Rayleigh length. The generalized space-time walk-off length, ℓ_{st} defines the effective interaction length limited by spatial walk-off and group velocity dispersion,

$$\ell_{st} = \left[\frac{\rho^2}{w_0^2} + \frac{\ln(2)(\alpha^2+16)\beta^2}{8t_p^2}\right]^{-1/2}. \qquad \text{(S.2)}$$

Here ρ is the spatial walk-off angle of the extraordinary ray, w_0 the Gaussian beam waist radius, and β is the group velocity mismatch between the fundamental and second harmonic waves. The parameter α the represents the temporal chirp of the fundamental beam given by $t_p = t_0\sqrt{1+\alpha^2}$ where t_0 is the Fourier transform-limited pulse width.

In our microscope, the focusing objective has an effective focal length of 20 mm. With an incident full-width half-maximum fundamental beam spatial width of 3mm, we estimate that the focused beam waist at approximately $w_0 = 2\ \mu m$, resulting in a Rayleigh length of approximately $26\ \mu m$. The transform limit pulse width of the fundamental beam is 85 fs. Despite precompensation, the beam broadens to roughly 100 fs at the objective focus, yielding a chirp parameter $\alpha \approx 0.62$. For type I phase matching at the fundamental wave of 800nm the spatial walk-off angle ρ is 68 milliradians. [2] From these parameters, we estimate the generalized space-time walk-off length is, $\ell_{st} \approx 30\ \mu m$.

Second harmonic generation from the Boc-*p*NPhe*p*NPhe crystal differs significantly as the estimated crystal thickness is only 0.5 μm, smaller than the incident wavelength. Since phase matching and spatial walk-off are negligible over this length scale, the second harmonic generation efficiency for the Boc-*p*NPhe*p*NPhe crystal can be described using the standard plane-wave approximation,

$$\epsilon = \frac{[2\omega d_{eff}]^2}{n_\omega n_{2\omega} \lambda_0 c^3 \varepsilon_0} \sqrt{\frac{2\,ln\,2}{\pi}} \frac{U_\omega L^2}{2 z_R t_p}. \quad \text{(S.3)}$$

Taking the ratio between $U_{2\omega}^{xtal}$ and $U_{2\omega}^{BBO}$ allows us to estimate the effective nonlinear susceptibility for the Boc-*p*NPhe*p*NPhe crystal

$$d_{eff}^{xtal} \approx d_{eff}^{BBO} \pi^{3/4} \left(\frac{U_\omega^{BBO}}{U_\omega^{xtal}}\right) \sqrt{\frac{U_{2\omega}^{xtal}}{U_{2\omega}^{BBO}}} \frac{\sqrt{z_R \ell_{S-T}^{BBO}}}{L_{xtal}}. \quad \text{(S.4)}$$

In deriving this equation, we have neglected small differences in the refractive indices for the BBO and Boc-*p*NPhe*p*NPhe crystals. For the BBO crystal, an average incident power of 0.5 mWatts and an integration time of 2.5 ms yielded a maximum acquired signal of $S_{2\omega}^{BBO} \approx 2.4\times10^6$ counts. These "counts" correspond to the number of photoelectrons excited by the second harmonic light integrated over the second harmonic spectrum during a time window equal to the "integration time". Comparatively, the maximum observed signal for the Boc-*p*NPhe*p*NPhe crystal at normal incidence, using an average incident power of 5 mW and a 250 ms integration time, was $S_{2\omega}^{xtal} \approx 1.6\times10^5$ counts. Using the established effective nonlinear susceptibility for BBO[2], $d_{eff}^{BBO} = 2.0\,pm/V$, and recognizing that the acquired second harmonic signals are proportional to $S_{2\omega} \sim U_{2\omega}\tau$ with τ being the detector integration time we estimate that the effective second-order nonlinear susceptibility for the Boc-*p*NPhe*p*NPhe crystals is 0.67 pm/V. Given that these measurements were conducted at normal incidence without angle optimization, this value represents a lower bound estimate of the material's nonlinear optical response.

References

1. H. Wang and A. M. Weiner, *IEEE J. Quantum Elect.*, 2003, **39**, 1600-1618.
2. SNLO nonlinear optics code available from A. V. Smith, AS-Photonics, Albuquerque, New Mexico, U.S.A.