

Supporting Information For

Crystal structures, photophysical properties and significant different two-photon excited fluorescence of the *trans*- and *cis*-oligo(phenylene vinylene)

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1. Experimental

1.1 Materials and apparatus

All chemicals were purchased as reagent grade and used without further purification. The solvents were dried and distilled according to standard procedures. ¹H NMR spectra were performed on a Bruker 400 Hz Ultrashield spectrometer and were reported as parts per million (ppm) from TMS (δ) and ¹³C NMR spectra were obtained on a Bruker Avance 100 MHz NMR spectrometer. IR spectra were recorded on NEXUS 870 (Nicolet) spectrophotometer in the 400-4000 cm⁻¹ region using a powder sample on a KBr plate.

1.2 Optical measurements

The linear spectra measurement:

All the solvents used for absorption and fluorescence measurements were HPLC grade. For dilute solutions of $c = 5.0 \times 10^{-6}$ M, in quartz cuvettes of 1 cm path length, one-photon absorption (OPA) spectra were recorded on a UV-265 spectrometer. One-photon excited fluorescence (OPEF) spectra were recorded on a PerkinElmer LS55 fluorescence spectrometer equipped with a 450 W Xe lamp. The concentrations are 5.0×10^{-6} mol/L. The linear emission spectra, fluorescence quantum yields and lifetime fluorescence were performed using Horiba Fluoro Max-4P fluorescence spectrophotometer.

Fluorescence lifetime measurement: The fluorescence lifetime was measured using the time-correlated single-photon-counting (TCSPC) technique (Horiba) with excitation source NanoLed® 375 nm impulse repetition rate 1 MHz (Horiba) at 90 °C to the R928P detector (Hamamatsu Photonics, Japan). The detector was set to 453 nm with a 10 nm bandpass. The electrical signal was amplified by TB-02 pulse amplifier (Horiba) and the amplified signal was fed to the constant fraction discriminator CFD (Philips, The Netherlands). The first detected photon was used as a Start signal by time-to-amplitude converter (TAC), the excitation pulse triggered the Stop signal. The multichannel analyzer (MCA) recorded repetitive start-stop signals from the TAC and generated a histogram of photons as a function of time-calibrated channels (6.88 ps/channel) until the peak signal reached 10000 counts. The lifetime was recorded on a 50 ns scale. The instrument response function was obtained using Rayleigh scatter of SiO₂ nanocrystals in H₂O sample in a quartz cuvette at 377 nm emission. The measurements were conducted at room. DAS6 v6.1 decay analysis software (Horiba) was used for lifetime calculations. The goodness of fit was judged by chi-squared values ($\chi^2 \approx 1$) (Table S2), Durbin-Watson parameters and visual observations of fitted line, residuals and autocorrelation function. One exponential decay equations were used for *trans*-1/2 data fitting and three-exponential decay equations were used for *cis*-1/2 data fitting which discovered that there might exist three components in the excited state and each component has its inherent OPEF lifetime and the emission processes of *cis*-1 was

displayed in Fig.S5. All samples were analyzed in triplicates using new solutions to avoid reanalyzing the same sample.

TPA cross-sections:

The two-photon fluorescence spectra of compounds in THF with $c = 1.0 \times 10^{-3}$ mol/L were measured using femtosecond laser pulse and Ti: sapphire system (680–840 nm, 80 MHz, 140 fs, Chameleon II) as the light source. All measurements were carried out in air at room temperature. Thus, the δ values of samples were determined by the following Equation (1). $\delta_s = \delta_r \cdot F_s \cdot \Phi_r \cdot C_r \cdot n_r / (F_r \cdot \Phi_s \cdot C_s \cdot n_s)$ where the subscripts “s” and “r” represent sample and reference (here, fluorescein in ethanol solution at a concentration of 1.0×10^{-3} mol/L was used as reference), respectively. F is the overall fluorescence collection efficiency intensity of the fluorescence signal collected by the fiber spectra meter. Φ , n and c are the quantum yield of the fluorescence, the refractive index of solvent, and the concentration of the solution, respectively.

1.3. X-ray crystallography

The crystal structures were determined by single crystal X-ray analyses. Data collections were performed using a Siemens SMART CCD area detector diffractometer with Mo/K α radiation with an ω -scan mode [$\lambda = 0.71073$ Å]. The structures were solved with direct methods using the SHELXTL program^[1] and refined anisotropically with SHELXTL using full-matrix least squares procedure. All non-hydrogen atoms were refined anisotropically. Crystal data and experimental details for the complexes are listed in Table S1. Additional crystallographic details and complete listings of the compounds have been deposited with the Cambridge Crystallographic Data Center as supplementary publications with reference number CCDC 737793 for *trans*-**1**^[2], 855787 for *cis*-**1**, 855789 for *trans*-**2**, 855788 for *cis*-**2** (Copies of the data can be obtained free of charge CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

2 Syntheses and discussion

2.1 Syntheses of *trans/cis*-**1**

2,5-Dibutoxy-1,4-bis(triphenylphosphonium)benzene dichloride (2.11 g, 2.5 mmol) and picolinaldehyde (1.07 g, 10 mmol), fresh *t*-BuOK (2.25 g, 20 mmol) were crashed together with a pestle and mortar at room temperature for 0.5 h. Separation of *cis*- and *trans*-isomers was accomplished by radial chromatography technique using a Chromatotron apparatus and petroleum/ethyl acetate (8:1) as the eluting solvent. Single crystals of the *trans*- and *cis*-isomers were grown slowly by evaporating solutions with acetone and ethanol solvents, respectively.

trans-**1**: ¹H NMR (CDCl₃, 400 MHz) δ 8.60 (d, $J = 4.8$ Hz, 2 H), 7.91 (d, $J = 16$ Hz, 2 H), 7.74 (t, $J = 7$ Hz, 2 H), 7.56 (d, $J = 7.6$ Hz, 2 H), 7.39 (d, $J = 16$ Hz, 2 H), 7.17-7.21 (M, 4 H), 4.08 (t, $J = 6.4$ Hz, 4H), 1.84-1.91 (m, 4 H), 1.53-1.62 (m, 4 H), 1.03 (t, $J = 7.4$ Hz, 6 H). ¹³C NMR (100 MHz) δ 13.95, 19.41, 30.93, 68.67, 111.31, 121.37, 121.82, 126.65, 127.74, 129.04, 136.47, 149.54, 151.38, 156.35. MALDI-TOF MS: ($[M + H]^+$), 429.26. FT-IR (KBr, cm⁻¹): 3430, 2956, 2937, 2869, 1629, 1582, 1499, 1474, 1424, 1392, 1345,

1310, 1236, 1012, 992, 858, 773, 743, 613. Melting point: 193.1 °C.

cis-1: ¹H NMR (CDCl₃, 400 MHz) δ 8.60 (d, J = 4.8 Hz, 2 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.28 (d, J = 8 Hz, 2 H), 7.09 (t, J = 6 Hz, 2 H), 6.92 (d, J = 12 Hz, 2 H), 6.75 (s, 2 H), 6.72 (d, J = 12 Hz, 2 H), 3.57 (t, J = 6.4 Hz 4H), 1.50-1.57 (m, 4 H), 1.28-1.38 (m, 4 H), 0.87 (t, J = 7.4 Hz, 6 H). ¹³C NMR (100 MHz) δ 13.75, 19.13, 31.18, 68.46, 114.14, 121.58, 124.06, 126.04, 128.95, 129.98, 135.68, 149.16, 150.23, 156.7. MALDI-TOF MS: ([M + H]⁺), 429.25.. FT-IR (KBr, cm⁻¹): 3451, 2959, 2934, 2876, 1625, 1582, 1486, 1461, 1427, 1401, 1376, 1306, 1279, 1192, 1147, 1118, 1041, 993, 906, 872, 823, 803, 743, 633, 544. Melting point: 95.6 °C.

2.2 Syntheses of *trans/cis-2*

2,5-bis[(S)-2-methylbutoxy]-1,4-bis(triphenylphosphonium)benzene dichloride (2.18 g, 2.5 mmol) and picolinaldehyde (1.07 g, 10 mmol), fresh *t*-BuOK (2.25 g, 20 mmol) were crashed together with a pestle and mortar at room temperature for 0.5 h. Separation of *cis*- and *trans*-isomers was accomplished by radial chromatography technique using a Chromatotron apparatus and petroleum/ethyl acetate (8:1) as the eluting solvent. Single crystals of the *trans*- and *cis*-isomers were grown slowly by evaporating solutions with acetone and ethanol solvents, respectively.

trans-2: ¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, J = 4.8 Hz, 2 H), 7.91 (d, J = 16 Hz, 2 H), 7.74 (t, J = 7.6 Hz, 2 H), 7.55 (d, J = 7.6 Hz, 2 H), 7.40 (d, J = 16 Hz, 2 H), 7.19 (m, 4 H), 3.42 (m, 2 H), 3.34 (m, 2 H), 1.65 (m, 2 H), 1.38 (m, 2 H), 1.13 (m, 2 H), 1.12 (d, J = 6.8 Hz, 6 H), 0.85 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ 156.43, 151.47, 149.60, 136.41, 129.18, 127.66, 126.60, 121.79, 121.15, 111.25, 74.09, 34.93, 26.33, 16.87, 11.41. MALDI-TOF MS: ([M + H]⁺), 457.26. FT-IR (KBr, cm⁻¹): 3450, 3045, 2963, 2916, 2872, 1629, 1582, 1559, 1497, 1472, 1419, 1391, 1345, 1310, 1203, 1151, 1031, 987, 856, 773, 746, 728, 612, 518.

cis-2: ¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, J = 4.4 Hz, 2 H), 7.53 (m, 2 H), 7.31 (d, J = 8 Hz, 2 H), 7.12 (t, J = 5.6 Hz, 2 H), 6.96 (d, J = 12 Hz, 2H), 6.75 (d, J = 12 Hz, 2 H), 6.74 (s, 2 H), 3.96 (t, J = 6.4 Hz, 2 H), 3.87 (t, J = 7.6 Hz, 2 H), 2.01 (m, 2 H), 1.65 (m, 2 H), 1.38 (m, 2 H), 1.12 (d, J = 6.8 Hz, 6 H), 1.02 (t, J = 7.2 Hz, 6 H). ¹³C NMR (100 M, Hz, CDCl₃) δ 156.86, 150.28, 149.38, 135.54, 130.08, 128.68, 125.91, 124.07, 121.53, 114.03, 73.55, 34.49, 26.03, 16.48, 11.20. MALDI-TOF MS: ([M + H]⁺), 457.28. FT-IR (KBr, cm⁻¹): 3450, 2968, 2923, 2876, 2851, 1623, 1584, 1561, 1493, 1462, 1425, 1384, 1298, 1206, 1183, 1143, 1047, 1013, 878, 816, 782, 747, 718, 617, 537.

2.3 Discussion

Trans-isomers and *cis*-isomers were obtained by solid-phase reaction in good yield (*trans*- = *cis*- ≈ 40%), but in (CH₃)₃COK/(CH₃)₃COH solvent system, we only obtained the *trans*-isomer in 70% yield. The ¹H NMR spectrums of *trans/cis-1* show two resonances for olefinic Protons: two doublets at δ 7.39, 7.91 for *trans-1* and 7.40, 7.93 for *trans-2* with coupling constants of 16 Hz

typical for a *trans* vinylene configuration and two doublets at δ 6.72, 6.92 for *cis-1* and 6.75, 6.96 for *cis-2* with coupling constants of 12 Hz typical for a *cis* vinylene configuration. The chemical shifts of the olefinic in the *trans*-conformations are larger than those in the *cis*-conformations, because *trans*-conformations exhibits more planarity and a greater conjugated effect in the vinyl benzene direction than that of the *cis*-conformations, which are the decreased shielding effect of the phenyl ring on the olefinic protons and the decreased electron cloud density on the olefinic segments.

3. Figures and tables

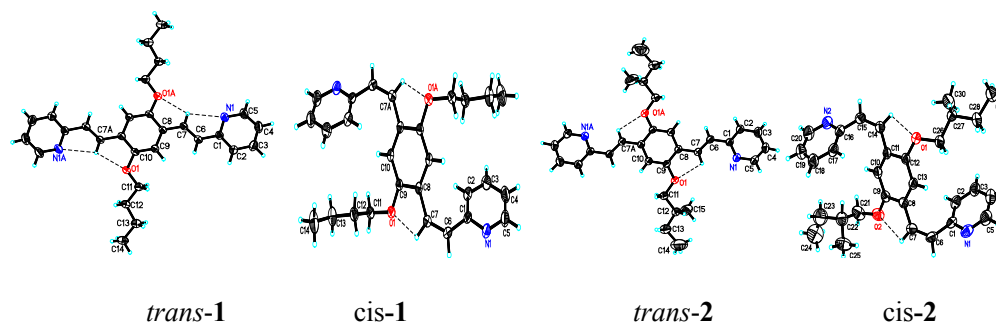


Fig. S1 The structure of *trans/cis-1* and *trans/cis-2* showing the intra-hydrogen bonds and atom-numbering scheme for the contents of the asymmetric unit.

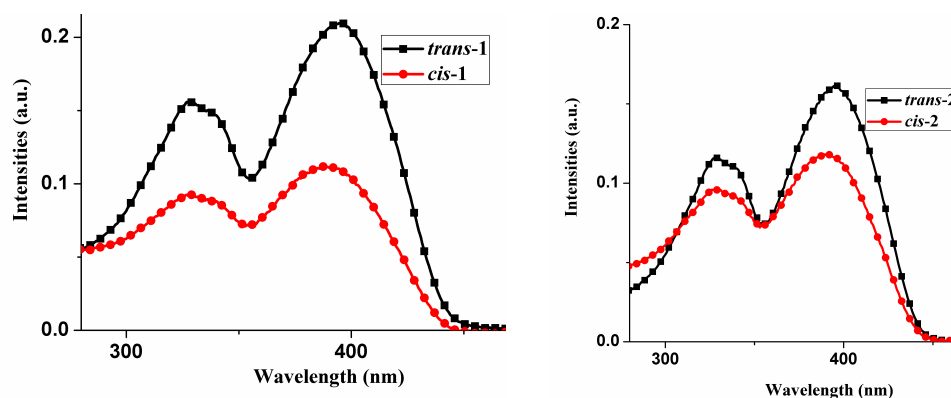


Fig. S2 The linear absorption spectra of *trans/cis-1* and *trans/cis-2* in THF.

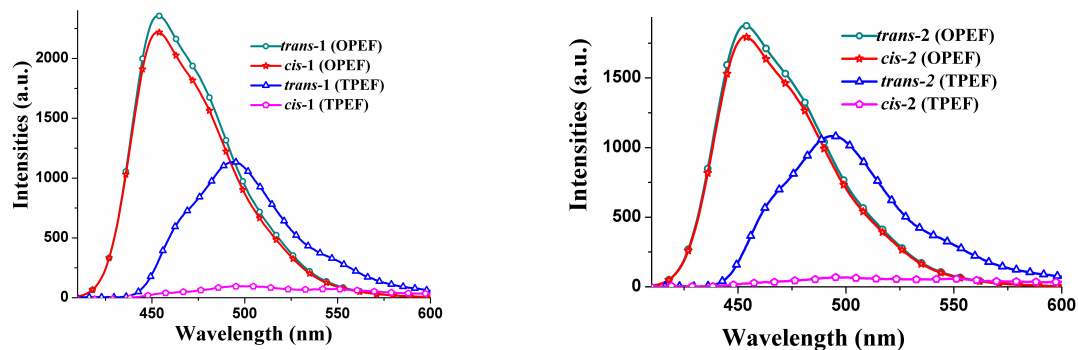


Fig. S3 One-photon excited fluorescence ($\lambda_{\text{ex}} = 396$ nm) and two-photon excited fluorescence ($\lambda_{\text{ex}} = 690$ nm) of *trans/cis-1* (left) and *trans/cis-2* (right) in THF solution with a solution concentration of 5.0×10^{-6} and 1.0×10^{-3} mol/L, respectively.

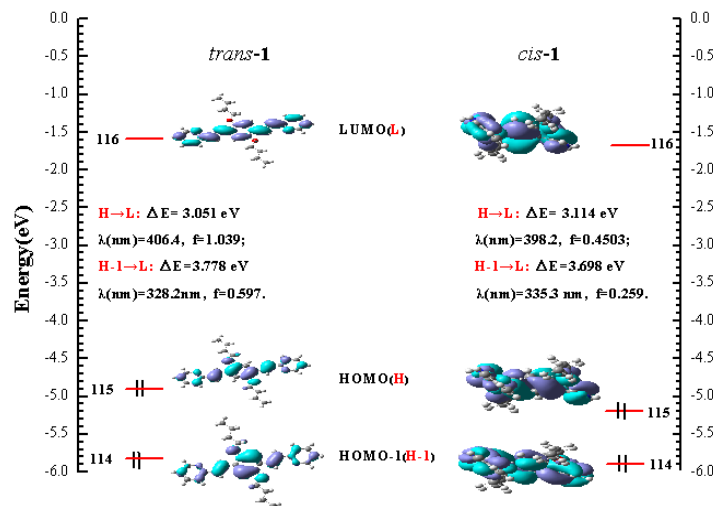


Fig. S3 Molecular orbital energy diagram of *trans*-1 (left) and *cis*-1 (right) in the ground state.

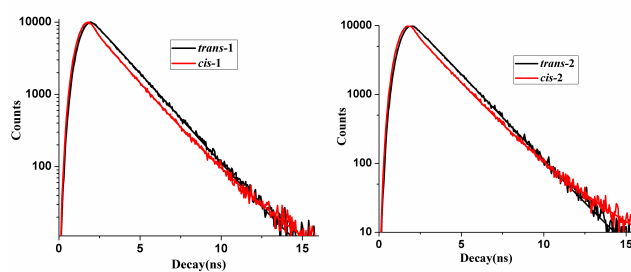


Fig. S4 Time-resolved fluorescence curves of *trans/cis*-1 and *trans/cis*-2 in THF.

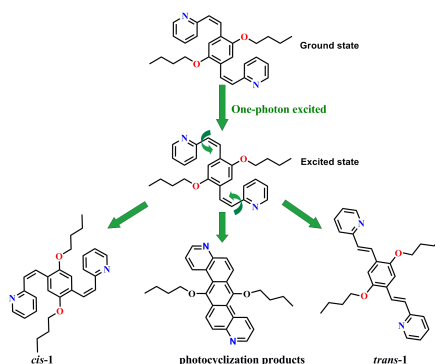


Fig. S5 Schematic of photochemical and emission processes of *cis*-1 by one-photon excited in THF solution.

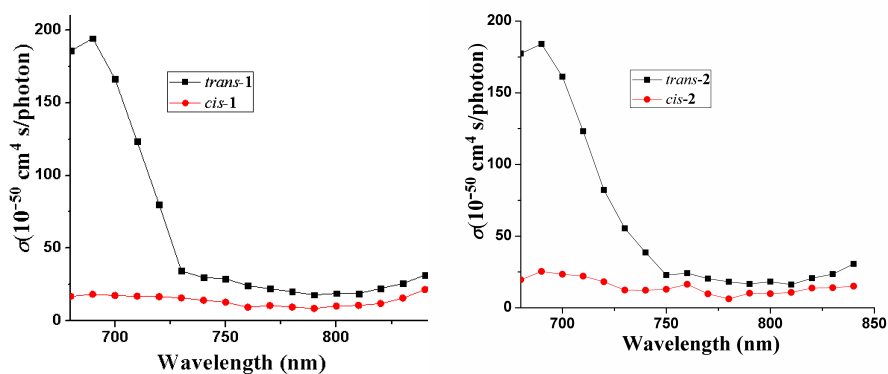


Fig. S6 Two-photon (from a 140 fs, 76 MHz Ti:sapphire laser) absorption cross sections of *trans/cis*-1 (left) and *trans/cis*-2 (right) in THF vs excitation wavelengths of identical energy of 0.300 W.

Table S1 Crystallographic data for *trans*-isomers and *cis*-isomers

Compound	<i>trans</i> -1	<i>cis</i> -1	<i>trans</i> -2	<i>cis</i> -2
Chemical formula	C ₂₈ H ₃₂ N ₂ O ₂	C ₂₈ H ₃₂ N ₂ O ₂	C ₃₀ H ₃₆ N ₂ O ₂	C ₃₀ H ₃₆ N ₂ O ₂
Formula Mass	428.56	428.56	456.61	456.61
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
<i>a</i> /Å	8.8822(18)	9.0577(16)	9.735(7)	9.2930(15)
<i>b</i> /Å	13.892(3)	8.8169(15)	13.866(10)	14.162(2)
<i>c</i> /Å	10.387(2)	16.292(3)	10.782(8)	10.4495(18)
α /°	90.00	90.00	90.00	90.00
β /°	107.392(2)	113.972(8)	113.771(9)	104.566(2)
γ /°	90.00	90.00	90.00	90.00
Unit cell volume/Å ³	1223.1(4)	1188.9(4)	1331.9(17)	1331.1(4)
Temperature/K	298(2)	298(2)	296(2)	296(2)
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)
No. of formula units per unit cell, <i>Z</i>	2	2	2	2
No. of reflections measured	8512	6699	7263	6620
No. of independent reflections	2162	2209	2339	4008
<i>R</i> _{int}	0.0395	0.0318	0.0372	0.0238
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.0488	0.0443	0.1059	0.0665
Final w <i>R</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1316	0.1087	0.3294	0.1950
Final <i>R</i> _{<i>I</i>} values (all data)	0.0817	0.0624	0.1279	0.0718
Final w <i>R</i> (<i>F</i> ²) values (all data)	0.1539	0.1217	0.3449	0.2037

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left[\frac{\sum w \cdot (F_o^2 - F_c^2)^2}{\sum w (F_o^2)^2} \right]^{1/2}, w = \left[\sigma^2(F_o) + (0.1(\max(0, F_o^2) + 2F_c^2)/3)^2 \right]^{-1}$$

Table S2 Photophysical data of all the compounds.

Compound	λ_{ex}^a	λ_{em}^b	τ^c (Fractional contribution)	χ^2	Φ^d	σ^e
<i>trans</i> -1	327, 395	453	1.73 (1.00)	1.24	33.5	193
<i>cis</i> -1	329, 390	453	1.63 (75.87), 0.18 (17.28), 3.17 (6.85)	0.95	33.8	30
<i>trans</i> -2	328, 395	453	1.73 (1.00)	1.09	35.7	184
<i>cis</i> -2	329, 391	453	1.63 (76.49), 0.17 (16.23), 3.17 (7.27)	0.95	36.3	25

^a Linear absorption maxima(nm). ^b Peak position of OPEF, excited at the absorption maximum. ^c Fluorescence lifetime (ns).

^d Quantum yields measured using HORIB FluoroMax-4P fluorescence spectrophotometer. ^e TPA cross-section (GM, 1 GM = 10⁻⁵⁰ cm⁴ s·photon⁻¹).

Table S3 The two-photon absorption cross section σ_{tp} ($\text{GM}=10^{-50}\text{cm}^4\text{s}/\text{photon}$), excitation E (eV), and the corresponding wavelength λ (nm) of the ten lowest excited states for *t trans-1* and *cis-1* in gas phase.

<i>trans-1</i>			<i>cis-1</i>		
E	λ	σ_{tp}	E	λ	σ_{tp}
3.11	795.21	0.00	3.46	714.77	0.00
3.82	647.41	1240.57	3.91	632.51	133.33
3.83	645.72	0.00	4.16	594.50	0.00
4.01	616.73	24.74	4.27	579.18	0.00
4.01	616.73	0.00	4.27	579.18	0.47
4.24	583.28	0.00	4.31	573.80	0.00
4.25	581.91	435.52	4.36	567.22	1.08
4.42	559.52	119.69	4.67	529.57	167.82
4.71	525.07	85.35	4.76	519.56	8.53
4.80	515.23	0.00	4.78	517.38	0.19

References:

- [1] G. M. Sheldrick. *Acta. Cryst. A.* 2008. **64**, 112..
[2] R. L. Zhang, Z. D. Liu, J. Y. Wu. *Acta Cryst.* 2010. **E66**, o1877.