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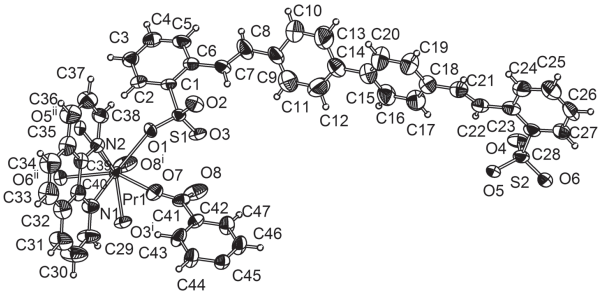
Crystal structure of the poly[(μ_4-biphenyl-4,4′-dicarboxylato-κ^4*O*:*O*′:*O*″:*O*‴) bis(μ_3-8-(11-(oxysulfonyl)-4-silbenyl)-2-(oxysulfonyl)stilbene-κ^4*O*:*O*′:*O*″,*O*‴) bis(1,10-phenanthroline-k^2*N*,*N*′) dipraseodymium(III)], $C_{94}H_{64}N_4O_{16}Pr_2S_4$



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Abstract

$C_{94}H_{64}N_4O_{16}Pr_2S_4$, monoclinic, $P2_1/c$ (no. 14), $a = 13.174(3)$ Å, $b = 21.479(4)$ Å, $c = 17.797(6)$ Å, $\beta = 124.23(2)°$, $V = 4163.6(19)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0599$, $wR_{ref}(F^2) = 0.1364$, $T = 293(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Yellow, block, size 0.10×0.14×0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.28 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω
$2\theta_{max}$:	54.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	37131, 9433
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5829
$N(param)_{refined}$:	541
Programs:	Diamond [6], SHELX [7], CrystalClear [8]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	4*e*	0.8656	0.0225	0.6605	0.052
H(3)	4*e*	1.0334	0.0436	0.8054	0.063
H(4)	4*e*	1.0784	0.1452	0.8560	0.067
H(5)	4*e*	0.9626	0.2257	0.7618	0.066
H(7)	4*e*	0.6924	0.2146	0.5376	0.066
H(8)	4*e*	0.8530	0.2988	0.6580	0.090
H(10)	4*e*	0.8215	0.3970	0.5670	0.130
H(11)	4*e*	0.5500	0.2939	0.5213	0.142
H(12)	4*e*	0.4110	0.3673	0.4214	0.165
H(13)	4*e*	0.6833	0.4676	0.4597	0.128
H(16)	4*e*	0.3072	0.4640	0.3858	0.097
H(17)	4*e*	0.1741	0.5386	0.2861	0.092
H(19)	4*e*	0.3961	0.5683	0.2050	0.087
H(20)	4*e*	0.5291	0.4950	0.3057	0.101
H(21)	4*e*	0.2074	0.6248	0.1292	0.065
H(22)	4*e*	0.0673	0.6190	0.1961	0.062
H(24)	4*e*	0.1319	0.7083	0.0602	0.078
H(25)	4*e*	0.0194	0.7889	−0.0368	0.091
H(26)	4*e*	−0.1657	0.8160	−0.0622	0.083
H(27)	4*e*	−0.2451	0.7606	0.0053	0.070
H(29)	4*e*	0.6197	0.1907	0.6454	0.084
H(30)	4*e*	0.6798	0.2710	0.7487	0.116
H(31)	4*e*	0.5649	0.2966	0.8029	0.100
H(33)	4*e*	0.3742	0.2762	0.8035	0.092
H(34)	4*e*	0.2034	0.2210	0.7533	0.091
H(36)	4*e*	0.0656	0.1288	0.6617	0.088
H(37)	4*e*	0.0339	0.0442	0.5743	0.082
H(38)	4*e*	0.1573	0.0258	0.5250	0.061
H(43)	4*e*	0.1976	0.0904	0.2257	0.070
H(44)	4*e*	0.0320	0.0874	0.0787	0.076
H(46)	4*e*	0.1165	−0.0855	0.0539	0.068
H(47)	4*e*	0.2866	−0.0811	0.2000	0.069

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The figure shows the asymmetric unit of the title structure. Tables 1–3 contain details of the methods used and a list of the atoms including atomic coordinates and displacement parameters.

Table 3: Fractional coordinates and atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr(1)	4*e*	0.39407(3)	0.07917(1)	0.51204(2)	0.0222(1)	0.0350(2)	0.0256(2)	0.0019(1)	0.0087(1)	−0.0029(2)
S(1)	4*e*	0.6794(1)	0.09387(6)	0.5145(1)	0.0322(7)	0.0344(8)	0.0346(9)	−0.0050(6)	0.0173(7)	−0.0075(6)
S(2)	4*e*	−0.1660(2)	0.66069(8)	0.1267(1)	0.0389(8)	0.0441(9)	0.047(1)	−0.0124(7)	0.0194(8)	−0.0117(8)
O(1)	4*e*	0.6830(4)	0.0262(2)	0.5049(3)	0.046(2)	0.025(2)	0.054(3)	−0.001(2)	0.018(2)	−0.011(2)
O(2)	4*e*	0.6804(4)	0.1278(2)	0.4458(3)	0.065(3)	0.057(3)	0.045(3)	−0.010(2)	0.035(3)	0.002(2)
O(3)	4*e*	0.5781(4)	0.1119(2)	0.5220(3)	0.029(2)	0.059(3)	0.049(3)	−0.010(2)	0.022(2)	−0.020(2)
O(4)	4*e*	−0.0972(4)	0.6771(2)	0.2214(4)	0.055(3)	0.071(3)	0.049(4)	−0.027(3)	0.026(3)	−0.022(3)
O(5)	4*e*	−0.1630(4)	0.5941(2)	0.1101(3)	0.037(2)	0.032(2)	0.045(3)	−0.008(2)	0.020(2)	−0.006(2)
O(6)	4*e*	−0.2968(4)	0.6794(2)	0.0741(4)	0.045(3)	0.038(2)	0.069(4)	−0.004(2)	0.028(3)	−0.009(2)
O(7)	4*e*	0.4505(4)	−0.0362(2)	0.3481(3)	0.040(3)	0.069(3)	0.036(3)	0.002(2)	−0.003(2)	0.011(2)
O(8)	4*e*	0.3733(4)	0.0428(3)	0.3790(4)	0.046(3)	0.122(5)	0.036(3)	−0.017(3)	0.019(3)	−0.030(3)
N(1)	4*e*	0.4703(5)	0.1667(2)	0.6387(4)	0.046(3)	0.055(3)	0.051(4)	−0.008(3)	0.032(3)	−0.010(3)
N(2)	4*e*	0.2735(5)	0.0938(2)	0.5894(4)	0.039(3)	0.042(3)	0.046(4)	0.002(2)	0.024(3)	0.000(2)
C(1)	4*e*	0.8130(5)	0.1119(3)	0.6220(4)	0.027(3)	0.044(3)	0.036(4)	−0.010(3)	0.018(3)	−0.014(3)
C(2)	4*e*	0.8851(5)	0.0635(3)	0.6804(5)	0.032(3)	0.056(4)	0.044(4)	−0.007(3)	0.022(3)	−0.006(3)
C(3)	4*e*	0.9849(6)	0.0759(3)	0.7672(5)	0.041(3)	0.059(4)	0.042(4)	−0.002(3)	0.014(3)	0.004(4)
C(4)	4*e*	1.0121(6)	0.1367(3)	0.7971(5)	0.043(4)	0.070(5)	0.037(5)	−0.009(4)	0.012(4)	−0.008(4)
C(5)	4*e*	0.9419(6)	0.1850(3)	0.7402(6)	0.046(4)	0.054(4)	0.061(6)	−0.018(3)	0.028(4)	−0.029(4)
C(6)	4*e*	0.8409(6)	0.1750(3)	0.6515(5)	0.036(3)	0.046(4)	0.045(5)	−0.009(3)	0.022(3)	−0.010(3)
C(7)	4*e*	0.7637(6)	0.2264(3)	0.5923(6)	0.048(4)	0.038(4)	0.071(6)	−0.012(3)	0.029(4)	−0.016(3)
C(8)	4*e*	0.7809(8)	0.2851(3)	0.6054(6)	0.094(6)	0.037(4)	0.062(6)	−0.005(4)	0.024(5)	−0.012(4)
C(9)	4*e*	0.6939(9)	0.3320(3)	0.5425(7)	0.078(6)	0.033(4)	0.110(8)	−0.006(4)	0.058(6)	−0.014(4)
C(10)	4*e*	0.738(1)	0.3885(5)	0.5328(9)	0.086(7)	0.079(7)	0.13(1)	0.015(6)	0.045(8)	0.023(7)
C(11)	4*e*	0.580(1)	0.3281(5)	0.5071(9)	0.099(8)	0.083(7)	0.15(1)	0.003(6)	0.052(9)	0.044(7)
C(12)	4*e*	0.4938(9)	0.3741(6)	0.446(1)	0.061(6)	0.127(9)	0.17(1)	0.001(6)	0.028(8)	0.070(9)
C(13)	4*e*	0.654(1)	0.4319(5)	0.4710(9)	0.105(8)	0.087(7)	0.14(1)	0.016(6)	0.072(9)	0.037(7)
C(14)	4*e*	0.5237(8)	0.4238(4)	0.4241(6)	0.085(6)	0.055(5)	0.063(6)	−0.006(5)	0.044(5)	0.002(4)
C(15)	4*e*	0.4354(8)	0.4718(4)	0.3587(6)	0.083(6)	0.060(5)	0.058(6)	0.006(4)	0.048(5)	−0.004(4)
C(16)	4*e*	0.3267(9)	0.4854(4)	0.3501(7)	0.094(7)	0.071(6)	0.096(8)	0.009(5)	0.064(7)	0.025(5)
C(17)	4*e*	0.2459(9)	0.5301(4)	0.2896(7)	0.086(6)	0.075(6)	0.097(8)	0.006(5)	0.068(7)	0.013(5)
C(18)	4*e*	0.2710(7)	0.5622(3)	0.2347(6)	0.068(5)	0.058(4)	0.056(5)	0.001(4)	0.041(5)	−0.006(4)
C(19)	4*e*	0.3775(8)	0.5478(4)	0.2419(6)	0.079(6)	0.088(6)	0.066(7)	0.019(5)	0.050(6)	0.020(5)
C(20)	4*e*	0.4577(9)	0.5036(4)	0.3027(7)	0.093(7)	0.095(7)	0.089(8)	0.031(6)	0.066(7)	0.030(6)
C(21)	4*e*	0.1878(7)	0.6102(3)	0.1688(6)	0.056(4)	0.062(4)	0.057(5)	−0.005(4)	0.039(4)	−0.009(4)
C(22)	4*e*	0.0907(6)	0.6345(3)	0.1593(5)	0.047(4)	0.054(4)	0.051(5)	−0.013(3)	0.027(4)	−0.002(3)
C(23)	4*e*	0.0149(6)	0.6845(3)	0.0952(5)	0.051(4)	0.055(4)	0.046(5)	−0.017(3)	0.024(4)	−0.009(3)
C(24)	4*e*	0.0568(7)	0.7186(4)	0.0503(6)	0.057(5)	0.065(5)	0.072(7)	−0.009(4)	0.036(5)	0.003(4)
C(25)	4*e*	−0.0107(9)	0.7670(4)	−0.0081(7)	0.091(7)	0.065(5)	0.079(7)	−0.012(5)	0.053(6)	0.003(5)
C(26)	4*e*	−0.1216(8)	0.7829(3)	−0.0237(6)	0.090(6)	0.037(4)	0.070(6)	−0.008(4)	0.039(6)	0.004(4)
C(27)	4*e*	−0.1689(7)	0.7501(3)	0.0172(6)	0.058(4)	0.049(4)	0.057(6)	−0.010(4)	0.026(4)	−0.012(4)
C(28)	4*e*	−0.1014(6)	0.7012(3)	0.0761(5)	0.047(4)	0.043(4)	0.043(5)	−0.017(3)	0.016(3)	−0.014(3)
C(29)	4*e*	0.5722(7)	0.2002(4)	0.6675(6)	0.054(5)	0.086(6)	0.079(7)	−0.032(4)	0.043(5)	−0.049(5)
C(30)	4*e*	0.6086(9)	0.2488(5)	0.7298(8)	0.087(6)	0.109(7)	0.115(9)	−0.049(6)	0.069(7)	−0.075(7)
C(31)	4*e*	0.5411(8)	0.2636(4)	0.7625(7)	0.095(7)	0.078(6)	0.082(7)	−0.030(5)	0.053(6)	−0.055(5)
C(32)	4*e*	0.4352(8)	0.2296(4)	0.7357(6)	0.074(5)	0.063(5)	0.050(5)	−0.001(4)	0.037(5)	−0.012(4)
C(33)	4*e*	0.3553(9)	0.2431(4)	0.7639(6)	0.102(7)	0.079(6)	0.070(7)	0.006(5)	0.060(6)	−0.024(5)
C(34)	4*e*	0.2548(9)	0.2098(4)	0.7352(7)	0.082(6)	0.090(6)	0.081(7)	−0.002(5)	0.062(6)	−0.020(5)
C(35)	4*e*	0.2239(7)	0.1571(4)	0.6769(6)	0.069(5)	0.069(5)	0.057(6)	0.011(4)	0.046(5)	0.003(4)
C(36)	4*e*	0.1199(8)	0.1197(4)	0.6456(7)	0.074(6)	0.094(6)	0.088(8)	−0.004(5)	0.067(6)	−0.007(5)
C(37)	4*e*	0.0998(8)	0.0707(4)	0.5922(7)	0.070(5)	0.074(6)	0.093(7)	−0.009(4)	0.065(6)	−0.003(5)
C(38)	4*e*	0.1754(6)	0.0592(3)	0.5639(5)	0.050(4)	0.047(4)	0.056(5)	−0.007(3)	0.030(4)	−0.003(3)
C(39)	4*e*	0.2985(6)	0.1432(3)	0.6458(5)	0.048(4)	0.045(3)	0.034(4)	0.004(3)	0.027(3)	0.004(3)
C(40)	4*e*	0.4037(6)	0.1804(3)	0.6742(5)	0.052(4)	0.046(4)	0.043(5)	0.002(3)	0.028(4)	−0.005(3)
C(41)	4*e*	0.3690(6)	0.0041(3)	0.3242(5)	0.032(3)	0.064(4)	0.026(4)	−0.010(3)	0.009(3)	0.004(3)
C(42)	4*e*	0.2613(5)	0.0048(3)	0.2281(4)	0.031(3)	0.058(4)	0.023(4)	0.000(3)	0.012(3)	−0.002(3)
C(43)	4*e*	0.1828(7)	0.0550(3)	0.1908(5)	0.057(4)	0.052(4)	0.030(4)	0.008(3)	0.002(4)	−0.010(3)
C(44)	4*e*	0.0832(7)	0.0529(3)	0.1028(5)	0.051(4)	0.055(4)	0.037(5)	0.014(3)	−0.003(4)	−0.008(3)
C(45)	4*e*	0.0555(5)	0.0009(3)	0.0477(4)	0.037(3)	0.052(4)	0.025(4)	0.000(3)	0.008(3)	−0.002(3)
C(46)	4*e*	0.1330(6)	−0.0492(3)	0.0874(5)	0.054(4)	0.055(4)	0.027(4)	0.015(3)	0.003(3)	−0.010(3)
C(47)	4*e*	0.2348(6)	−0.0468(3)	0.1757(5)	0.041(4)	0.068(5)	0.032(4)	0.015(3)	0.002(3)	−0.006(3)

Source of material

Into 8 mL of deionized water (444 mmol) 56 mg of Na_2L (L = disodium 4,4′-bis(2-sulfonatostyryl)biphenyl), 0.1 mmol, Aladdin), 18 mg of phen (1,10-phenantroline; 0.1 mmol), 24.2 mg of H_2bpdc (biphenyl-4,4′-dicarboxylic acid, 0.1 mmol, Aladdin), 44.5 mg of $Pr(NO_3)_3{\cdot}6H_2O$ (0.1 mmol) and one drop of triethylamine were added under stirring. After continually stirring for another 1 h, the mixture with the molar ratio of 1 $Pr(NO_3)_3{\cdot}6H_2O$: 1 Na_2L : 1 phen : 1 bpdc : 4440 H_2O was sealed into the autoclave, put into the oven and reacted at 423 °C for 3 days. After cooled to the room temperature and washed by methanol and chloroform, yellow block crystals were separated.

Experimental details

The carbon H-atoms were placed in calculated positions (C—H (phenyl ring) = 0.93 Å, C—H (ethylene of 4,4′-bis(2-sulfonatostyryl)bi-pheny) = 0.93 Å, and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Discussion

Among luminescence materials, the lanthanide luminescence is of very important owing to the luminescence quantum efficiency, luminescence brightness and line-like monochromaticity [1]. Because 4f-4f transition is forbidden, the luminescence of lanthanide complex is worked out by the energy transfer from the organic molecule located at excited state to lanthanide ion, which is called as 'antenna effect'. An aromatic carboxylate is an alternative to ligate lanthanide owing to the intense adsorption in the violet zone. The second ligand such as the 1,10-phenanthroline and its derivates are usually incorporated into the coordination system of lanthanide complexes to prevent the water coordination, which would influence the luminescence quantum efficiency and enhance the luminescence brightness by the synergic interaction with the first ligand [2–4]. In this work, a lanthanide complex with the composition $[Pr(phen)]_2{\cdot}L_2{\cdot}bpdc$ (L = 4,4′-bis(2-sulfonatostyryl)biphenyl and $bpdc$ = biphenyl-4,4′-dicarboxylic acid) , has been structurally determined. It is isostructural with the analog complexes of the lanthanides europium, gadolinium, terbium and dysprosium [5].

The asymmetric unit composes of one Pr(III) ion, one *phen*, one *L* and half of a *bpdc*, showing the neutral framework. Pr(III) is 8-coordinated by two N of one *phen* and six O of two *bpdc* offering two monodentate carboxylate groups and three sulfonyl groups composed of two oxygens of one bidentate and two oxygens of two monodentate. The distances of Pr—O and Pr—N range from 2.347 Å to 2.579 Å and from 2.641 Å to 2.660 Å, respectively. Adjacent Pr(III) are bridged by two caboxyls and two sulfonyls with 4.570 Å of Pr—Pr distance. The *bpdc* connects four Pr with the coordination mode $-\kappa^4O{:}O'{:}O''{:}O'''$ and *L* links three Pr with the coordination mode of $-\kappa^4O{:}O'{:}O''{:}O'''$. With the *phen* as the pendant adhered to the Pr, Pr-dimer as the node exhibits six-connection geometry containing four *L* and two *bpdc*. The six-connection node often occurs in MOF structure with bigger free void, such as IRMOFs and $Zn(BDC)(TED)_{0.5}$, and the coordination geometry is nearly octahedron. Comparably, coordination geometry of the six-connection node is violently distorted, which results in very small free void in spite of the existence of very long L ligand. The shorter distance of Pr—Pr is 13.218 Å along with *L* and 15.050 Å along with *bpdc*.

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