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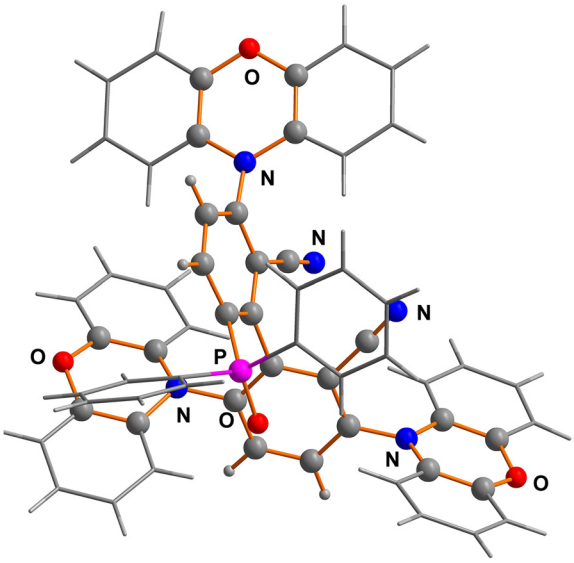
6-(Diphenylphosphoryl)-3,3′,6′-tris(10*H*-phenoxazin-10-*yl*)-[1,1′-biphenyl]-2,2′-dicarbonitrile, $C_{62}H_{38}N_5O_4P$



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Abstract

$C_{62}H_{38}N_5O_4P$, monoclinic, $P2_1/n$ (no. 14), a = 13.8942(6) Å, b = 16.1867(7) Å, c = 21.2705(8) Å, β = 97.716(2)°, V = 4740.4(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0401, $wR_{ref}(F^2)$ = 0.1066, T = 190 K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

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Table 1: Data collection and handling.

Crystal:	Red block
Size	0.09 × 0.06 × 0.05 mm
Wavelength:	Ga *K*α radiation (1.34139 Å)
μ:	0.63 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	53.9°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	27505, 8540, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6924
$N(param)_{refined}$:	729
Programs:	Bruker,[1] Olex2,[2] SHELX[3,4]

1 Source of materials

The starting material 6-fluoro-3,3′,6′-tri(10H-phenoxazin-10-yl)-[1,1′-biphenyl]-2,2′-dicarbonitrile was prepared according to literature.[5] 6-fluoro-3,3′,6′-tri(10H-phenoxazin-10-yl)-[1,1′-biphenyl]-2,2′-dicarbonitrile (2.29 g, 3.0 mmol), diphenylphosphane (0.37 g, 2.0 mmol) and caesium carbonate (0.98 g, 3.0 mmol) in *N*,*N*-dimethylformamide (DMF, 30 mL) was stirred and refluxed for 12 h. Cooling to room temperature, 10 mL hydrogen peroxide was added and stirred for half an hour. The mixture was diluted with 100 mL water, and extracted with ethyl acetate (3 × 30 mL). The combined organic layer was concentrated under reduced pressure and was further purified by silica gel column chromatography to red solid (1.56 g, 1.65 mmol, 55.0 % yield) and recrystallized from methanol and dichloromethane to obtain the red block crystals.

2 Experimental details

Using Olex2,[2] the structure was solved with the ShelXS[3] structure solution program using Direct Methods and refined with the ShelXL[4] refinement package.

3 Comment

TADF (thermally activated delayed fluorescence) materials typically adopt a D-π-A (donor-π spacer-acceptor) molecular architecture, which facilitates the reduction of the

singlet-triplet energy gap (Δ EST). Under thermal activation, these materials enable triplet excitons to participate in luminescence via reverse intersystem crossing (RISC), theoretically achieving 100 % internal quantum efficiency (IQE), making them highly promising candidates for next-generation display and lighting technologies.[6]

The title molecule employs phenoxazine as the electron donor and cyano/diphenylphosphine oxide (DPPO) groups as dual acceptors. Theoretical calculations reveal spatially separated frontier molecular orbitals: the HOMO is predominantly localized on the phenoxazine moiety, while the LUMO resides on the cyano and DPPO units. This minimal spatial overlap between HOMO and LUMO significantly reduces Δ EST, a critical feature for efficient TADF behavior.

Structurally, all bond lengths are in the expected ranges.

The N–C–C bond angles in the cyano groups are 176° and 178° respectively, approaching linear geometry. The C–P–O bond angles consistently measure 114°.

The dihedral angle between the two benzene rings in the biphenyl group is 79°, indicating significant torsional distortion. The phenoxazine moietes are all folded (see the figure). Thus, the dihedral angles between the phenoxazine core and adjacent benzene rings are 84°, 86°, and 89°, respectively. These pronounced torsional configurations–consistent with strategies reported in planarized D–A systems–disrupt π-conjugation and enforce spatial separation of charge densities, thereby suppressing non-radiative recombination pathways. In summary, this molecule has a certain application prospect in the field of luminescence and display.

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Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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