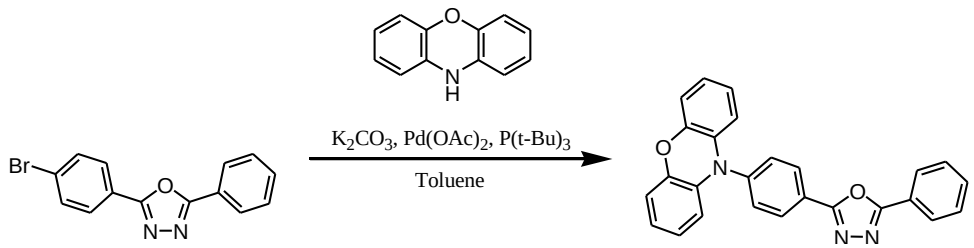
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Oxadiazole- and triazole-based highly-efficient thermally activated delayed fluorescence emitters for organic light-emitting diodes

Jiyoung Lee,[a] Katsuyuki Shizu,[b] Hiroyuki Tanaka,[b] Hiroko Nomura,[b]
Takuma Yasuda,[a,b,c] and Chihaya Adachi[b,c]

[a]Department of Automotive Science, Graduate School of Integrated Frontier Sciences,
Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan
[b]Center for Organic Photonics and Electronics Research (OPERA),
Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan
[c]International Institute for Carbon Neutral Energy Research (WPI-I2CNER),
Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan

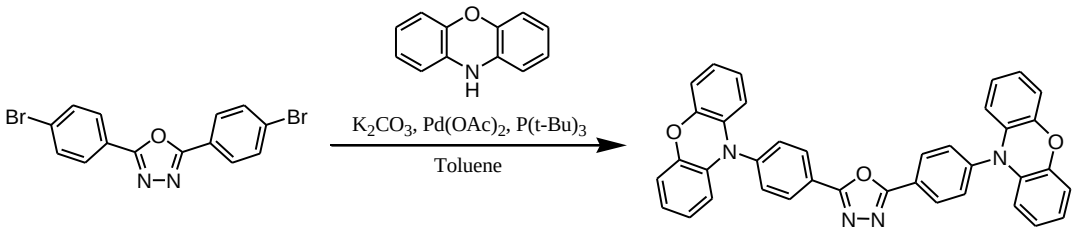
1. Preparation of 10-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl)-10H-phenoxazine (PXZ-OXD)



To a solution of 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (1.20 g, 3.98 mmol, synthesized by a reported method[S1]), phenoxazine (802 mg, 4.38 mmol) and potassium carbonate (1.81 g, 13.1 mmol) in toluene (30 mL) was added, with stirring, a solution of palladium(II) acetate (29.2 mg, 0.13 mmol) and tri-*tert*-butylphosphine (97.1 mg, 0.48 mmol) in toluene (30 mL). The mixture was stirred and heated under reflux for one day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by column chromatography (eluent: toluene/ethyl acetate = 10:1) afforded 1.52 g of PXZ-OXD. The yield was over 94%. The compound was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]
^{1}H NMR ($CDCl_3$, 300 MHz) δ = 5.98(d, 2H), 6.64(t, 2H), 6.69(t, 2H), 6.72(d, 2H), 7.55(m, 5H), 8.17(d, 2H), 8.38(d, 2H); ^{13}C NMR ($CDCl_3$, 300MHz) δ = 113.3, 115.7, 121.9, 123.3, 127.0, 129.2, 129.7, 131.8, 131.9, 133.7, 142.4, 144.0.
^{1}H NMR spectrum is shown below.
[MS]
MALDI-MS *m/z* Calcd for $C_{26}H_{17}N_3O_2$: 403; found: 403.
[Element analysis]
Calcd for $C_{26}H_{17}N_3O_2$: C, 77.41; H, 4.25; N, 10.42; found: C, 77.58; H, 4.18; N, 10.42.

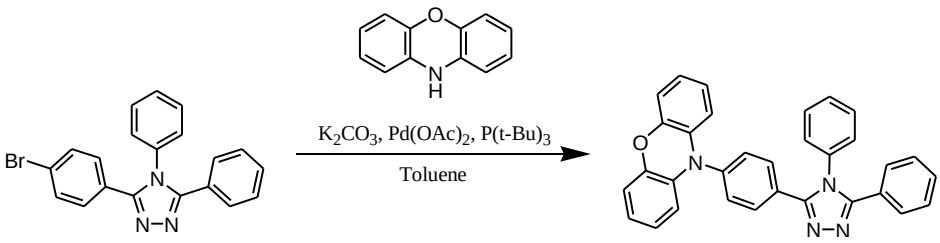
2. Preparation of 2,5-bis(4-(10H-phenoxazin-10-yl)phenyl)-1,3,4-oxadiazole (2PXZ-OXD)



To a solution of 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (630.8 mg, 1.66 mmol, synthesized by a reported method[S2]), phenoxazine (668.7 mg, 3.65 mmol) and potassium carbonate (1.52 g, 11.0 mmol) in toluene (25 mL) was added, with stirring, a solution of palladium(II) acetate (25.0 mg, 0.11 mmol) and tri-*tert*-butylphosphine (81.0 mg, 0.40 mmol) in toluene (25 mL). The mixture was stirred and heated under reflux for one day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by column chromatography (eluent: chloroform) afforded 965.2 mg of 2PXZ-OXD. The yield was over 99%. The compound was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]
^{1}H NMR ($CDCl_3$, 300 MHz) δ = 5.99(d, 4H), 6.61(t, 4H), 6.68(m, 8H), 7.57(d, 4H), 8.39(d, 4H); ^{13}C NMR ($CDCl_3$, 300MHz) δ = 113.3, 115.8, 121.9, 123.3, 129.7, 131.9, 133.7, 142.6, 144.0, 164.2.
^{1}H NMR spectrum is shown below.
[MS]
MALDI-MS *m/z* Calcd for $C_{38}H_{24}N_4O_3$: 584; found: 584.
[Element analysis]
Calcd for $C_{38}H_{24}N_4O_3$: C, 78.07; H, 4.14; N, 9.58; found: C, 78.02; H, 4.06; N, 9.56.

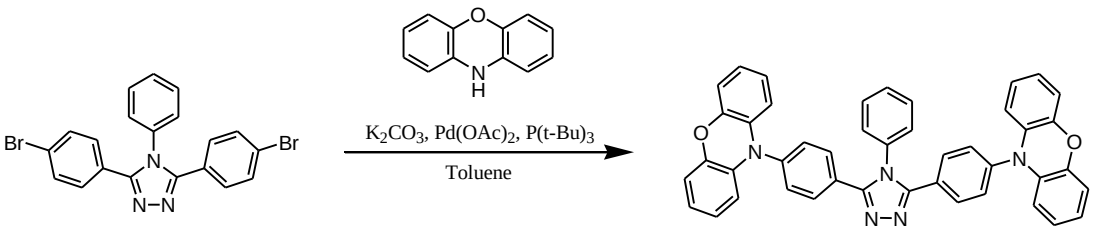
3. Preparation of 10-(4-(4,5-diphenyl-4H-1,2,4-triazol-3-yl)phenyl)-10H-phenoxazine (PXZ-TAZ)



To a solution of 3-(4-bromophenyl)-4,5-diphenyl-1,2,4-triazole (1.00 g, 2.66 mmol, synthesized by a reported method[S3]), phenoxazine (537 mg, 2.93 mmol) and potassium carbonate (1.21 g, 8.79 mmol) in toluene (20 mL) was added, with stirring, a solution of palladium(II) acetate (20.2 mg, 0.09 mmol) and tri-*tert*-butylphosphine (64.7 mg, 0.32 mmol) in toluene (20 mL). The mixture was stirred and heated under reflux for one day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by column chromatography (eluent: toluene/ethyl acetate = 1:1) afforded 1.01 g of PXZ-TAZ. The yield was over 79%. The compound was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]
^{1}H NMR (DMSO, 300 MHz) δ = 5.79(d, 2H), 6.67(t, 2H), 6.70(t, 2H), 6.74(d, 2H), 7.39(d, 2H), 7.41(m, 6H), 7.46(d, 2H), 7.52(d, 2H), 7.67(d, 2H); ^{13}C NMR ($CDCl_3$, 300MHz) δ = 113.2, 115.6, 121.6, 123.2, 126.7, 127.8, 128.5, 128.8, 129.8, 130.2, 131.0, 131.3, 133.9, 134.6, 140.4, 143.9.
^{1}H NMR spectrum is shown below.
[MS]
MALDI-MS *m/z* Calcd for $C_{32}H_{22}N_4O$: 478; found: 478.
[Element analysis]
Calcd for $C_{32}H_{22}N_4O$: C, 80.32; H, 4.63; N, 11.71; found: C, 80.21; H, 4.58; N, 11.70.

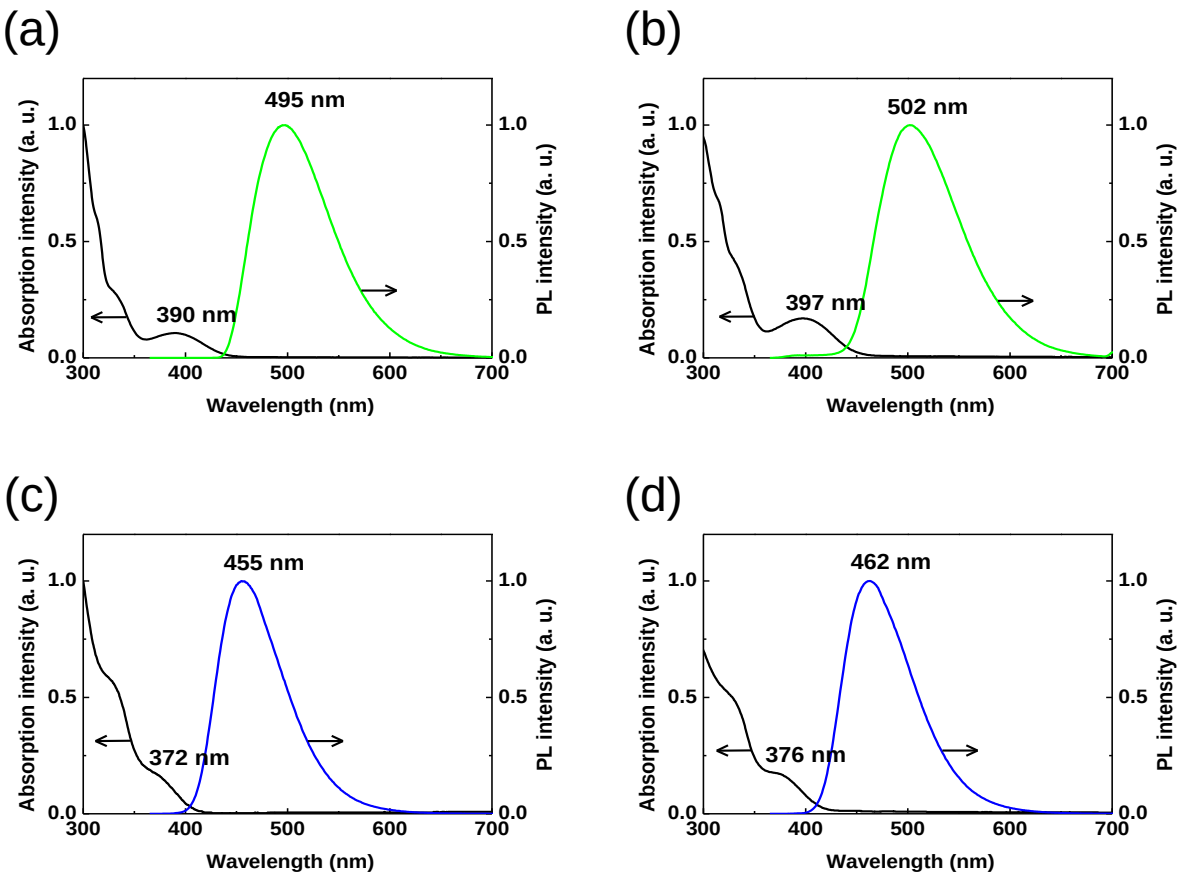
4. Preparation of 10,10'-((4-phenyl-4H-1,2,4-triazole-3,5-diyl)bis(4,1-phenylene))-bis(10H-phenoxazine) 2PXZ-TAZ



To a solution of 3,5-bis(4-bromophenyl)-4-phenyl-4H-1,2,4-triazole (1.50 g, 3.30 mmol, synthesized by a reported method[S1]), phenoxazine (1.33 g, 7.26 mmol) and potassium carbonate (3.01 g, 21.8 mmol) in toluene (40 mL) was added, with stirring, a solution of palladium(II) acetate (49.4 mg, 0.22 mmol) and tri-*tert*-butylphosphine (161.9 mg, 0.80 mmol) in toluene (40 mL). The mixture was stirred and heated under reflux for one day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by column chromatography (eluent: chloroform/hexane=1:4) afforded 1.52 g of 2PXZ-TAZ. The yield was over 70%. The compound was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]
^{1}H NMR ($CDCl_3$, 300 MHz) δ= 5.88(d, 4H), 6.57(t, 4H), 6.64(m, 8H), 7.30(m, 6H), 7.55(m, 3H), 7.68(d, 4H); ^{13}C NMR ($CDCl_3$, 300MHz) δ= 113.2, 115.6, 121.7, 123.2, 126.9, 127.8, 130.4, 131.1, 131.2, 133.8, 135.1, 140.5, 143.9, 154.3.
^{1}H NMR spectrum is shown below.
[MS]
MALDI-MS *m/z* Calcd for $C_{44}H_{29}N_5O_2$: 659; found: 659
[Element analysis]
Calcd for $C_{44}H_{29}N_5O_2$: C, 80.10; H, 4.43; N, 10.62; found: C, 80.11; H, 4.37; N, 10.61.

5. Ultraviolet-visible and photoluminescence spectra



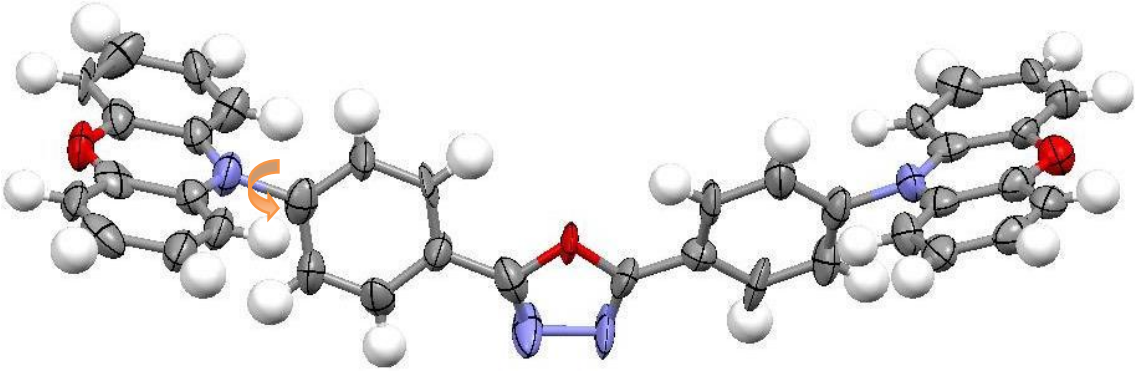
Supplementary Fig. S1: Ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectra of (a) PXZ-OXD, (b) 2PXZ-OXD, (c) PXZ-TAZ, and (d) 2PXZ-TAZ. UV-Vis spectra were measured using a UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan). PL spectra were measured using spectrofluorometers (Fluoromax-4, Horiba Jobin Yvon, USA; FP-6500-A-ST, Jasco, Japan). Excitation wavelength was 330 nm.

6. Calculated and experimental absorption and emission wavelengths

Supplementary Table S1: Absorption (λ_{ab}) and emission wavelengths (λ_{em}) for PXZ-OXD, 2PXZ-OXD, PXZ-TAZ, and 2PXZ-TAZ were computed using time-dependent density functional theory (TD-DFT) at the CAM-B3LYP/cc-pVDZ level of theory. Solvent effects were taken into account by means of the polarizable continuum model.

Compound	λ_{ab} (nm)		λ_{em} (nm)	
	Calc.	Exp.	Calc.	Exp.
PXZ-OXD	416	390	513	495
2PXZ-OXD	439	397	525	502
PXZ-TAZ	366	372	428	455
2PXZ-TAZ	370	376	438	462

7. ORTEP diagram of the crystalline structure of 2PXZ-OXD



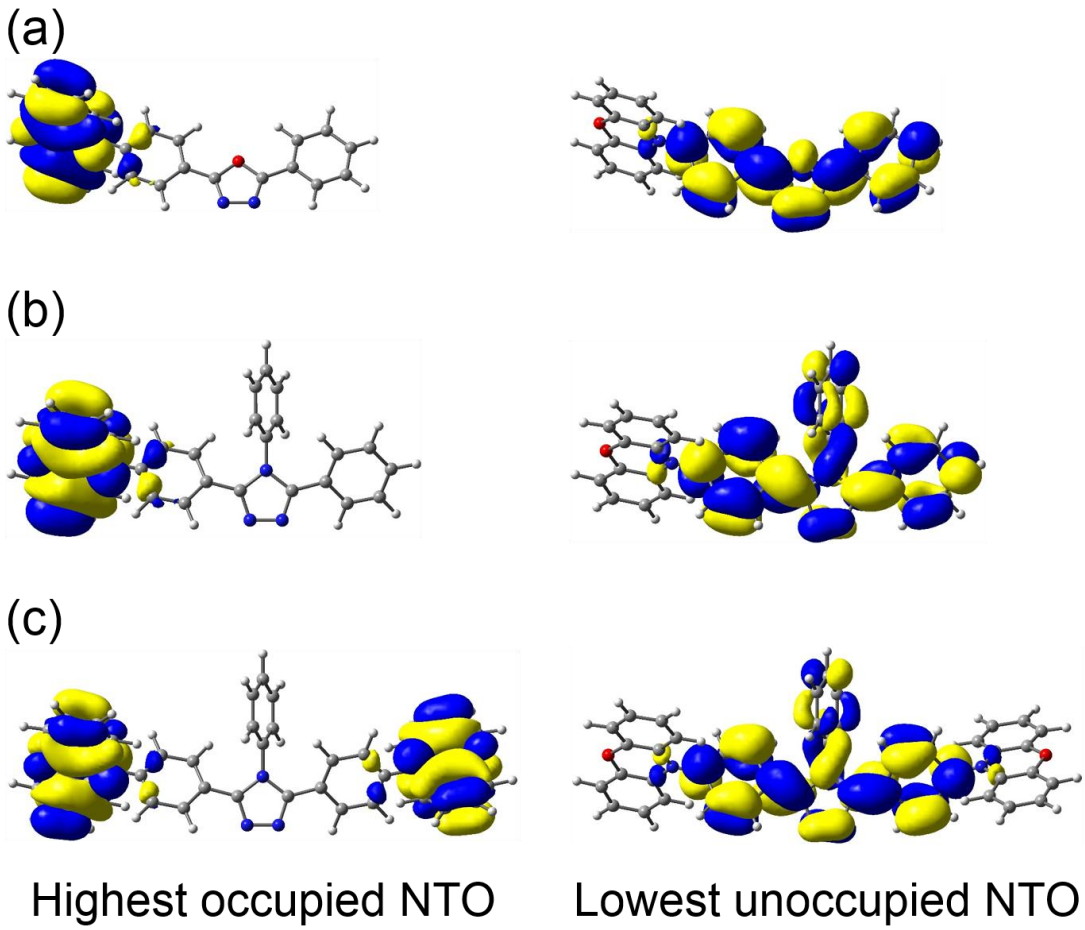
Supplementary Fig. S2: ORTEP diagram of the molecular structure of 2PXZ-OXD determined by single crystal X-ray diffraction. The torsion angle is 76.7°.

8. Calculated S_1 and T_1 excitation energies and ΔE_{ST}

Supplementary Table S2: Calculated S_1 and T_1 excitation energies and the difference between them (ΔE_{ST}) for PXZ-OXD, 2PXZ-OXD, PXZ-TAZ, and 2PXZ-TAZ. Calculation of ΔE_{ST} was carried out with TD-DFT at the CAM-B3LYP/cc-pVDZ level of theory. Oscillator strengths (f) of the S_1 states shown in parentheses.

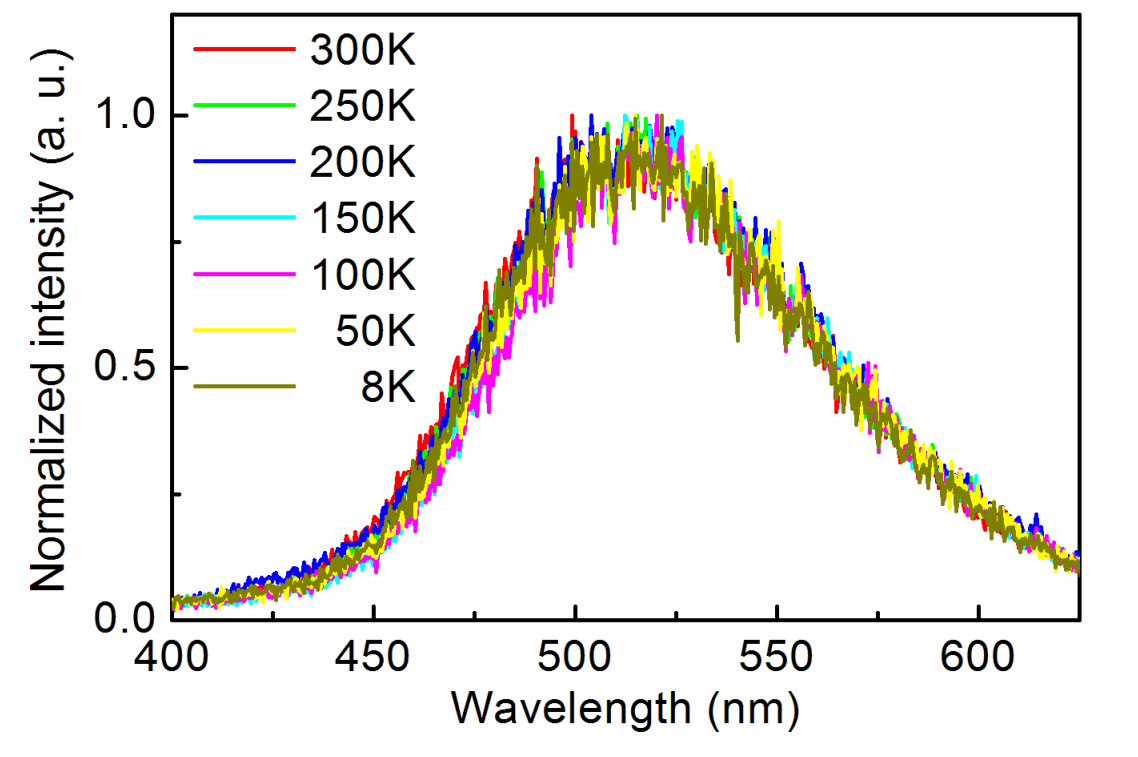
Compound	S_1 energy (eV)	T_1 energy (eV)	ΔE_{ST} (eV)
PXZ-OXD	3.49 (0.0001)	2.84	0.65
2PXZ-OXD	3.40 (0.0000)	2.83	0.57
PXZ-TAZ	3.80 (0.0000)	2.83	0.97
2PXZ-TAZ	3.69 (0.0000)	2.83	0.86

9. Highest occupied and lowest unoccupied natural transition orbitals for the S_1 states of PXZ-OXD, PXZ-TAZ, and PXZ-2TAZ



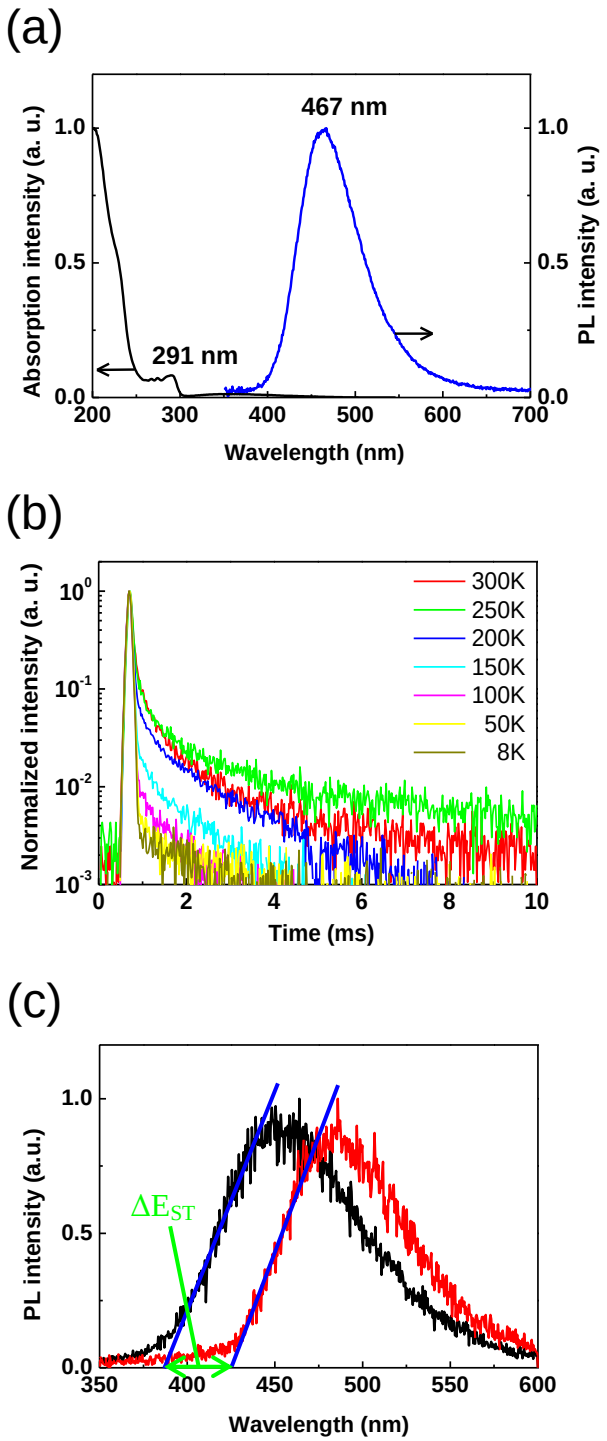
Supplementary Fig. S3: Highest occupied and lowest unoccupied natural transition orbitals (NTOs) for the S_1 states of (a) PXZ-OXD, (b) PXZ-TAZ, and (c) PXZ-2TAZ calculated at the CAM-B3LYP/cc-PVDZ level of theory.

10. Temperature dependence of photoluminescence spectrum of 6 wt% 2PXZ-OXD:DPEPO film



Supplementary Fig. S4: Temperature dependence of photoluminescence spectrum of a 6 wt% 2PXZ-OXD:DPEPO film.

11. Photoluminescence characteristics of 6 wt% 2PXZ-TAZ:DPEPO film



Supplementary Fig. S5: (a) Absorption and PL spectra of a 6 wt% 2PXZ-TAZ:DPEPO film. (b) Transient PL decay curves for the doped film measured at temperatures of 8 to 300 K. (c) Fluorescence and phosphorescence spectra of the doped film measured at 8 K. Black and red lines show fluorescence and phosphorescence spectra, respectively.

References

S1. W. Kwon, B. Ahn, D. M. Kim, Y.-G. Ko, S. G. Hahm, Y. Kim, H. Kim, and M. Ree, *J. Phys. Chem. C*, **115**, 19355-19363 (2011).

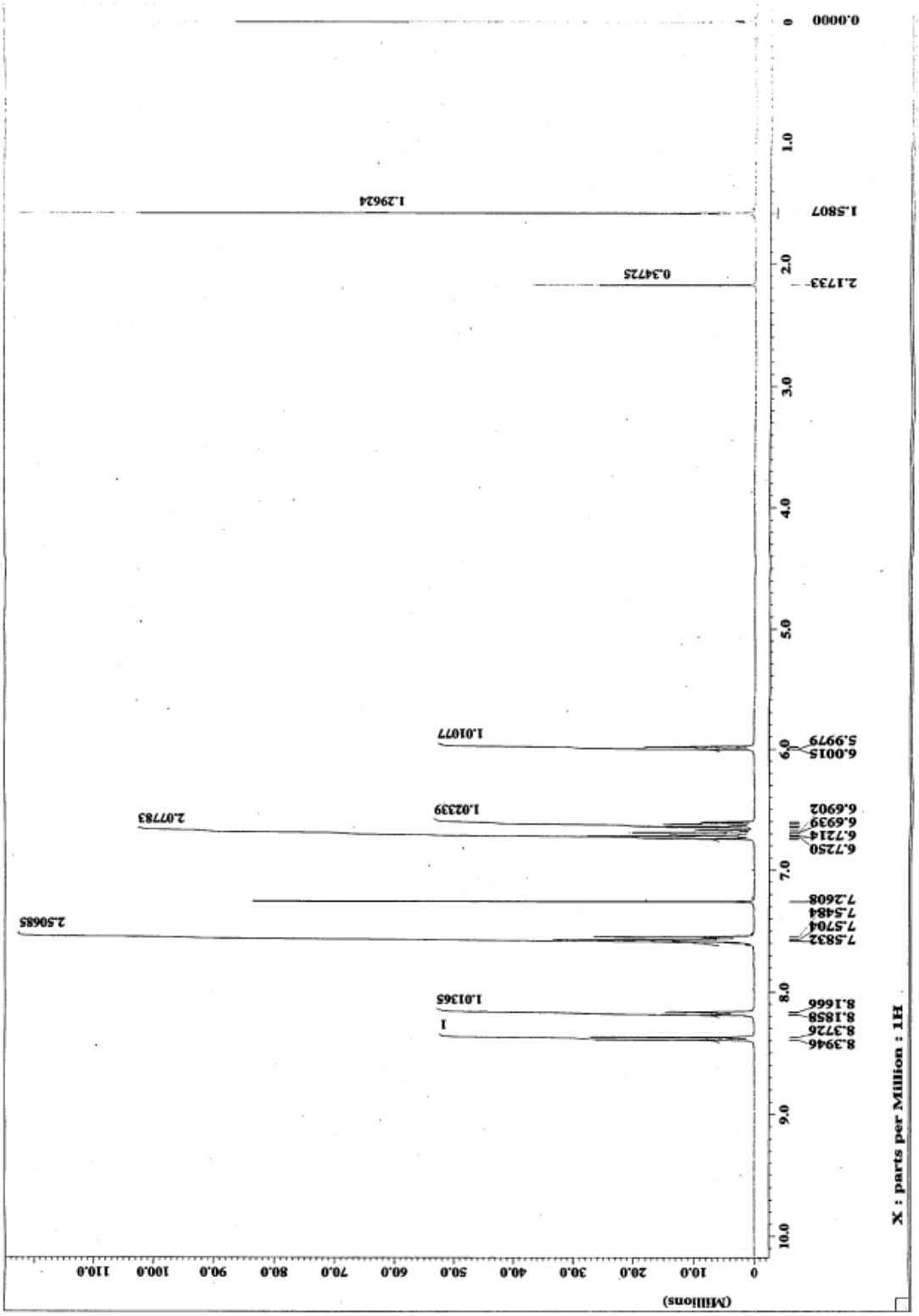
S2. X. J. Feng, P. L. Wu, K. F. Li, M. S. Wong, and K. W. Cheah, *Chem. Eur. J.* **17**, 2518-2526 (2011).

S3. S. Kwon, K.-R. Wee, A.-L. Kim, and S. O. Kang, *J. Phys. Chem. Lett.*, **1**, 295-299 (2010).

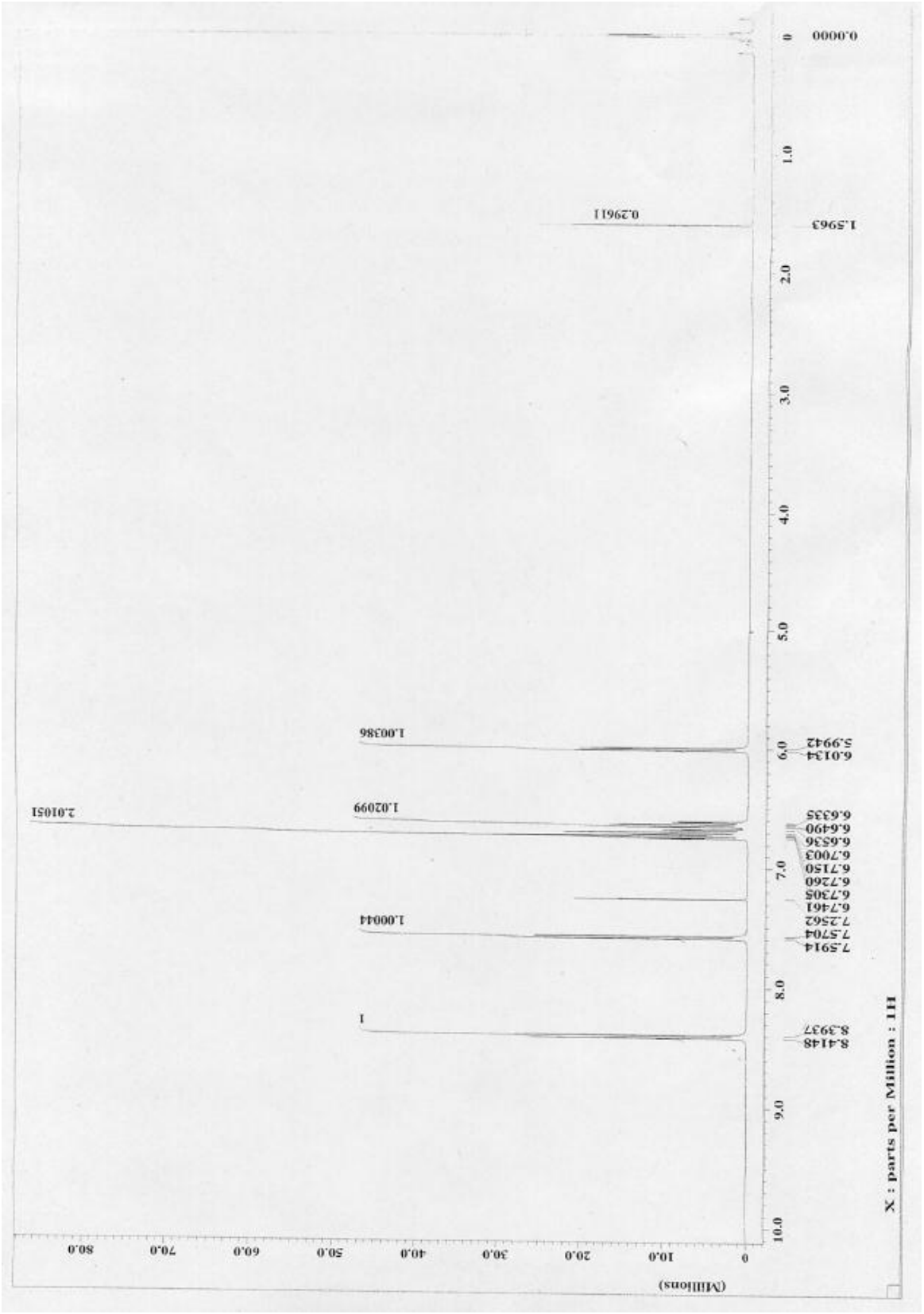
S4. W. Y. Wong and Y. H. Guo, *J. Mol. Struct.* **890**, 150-156 (2008).

Appendix

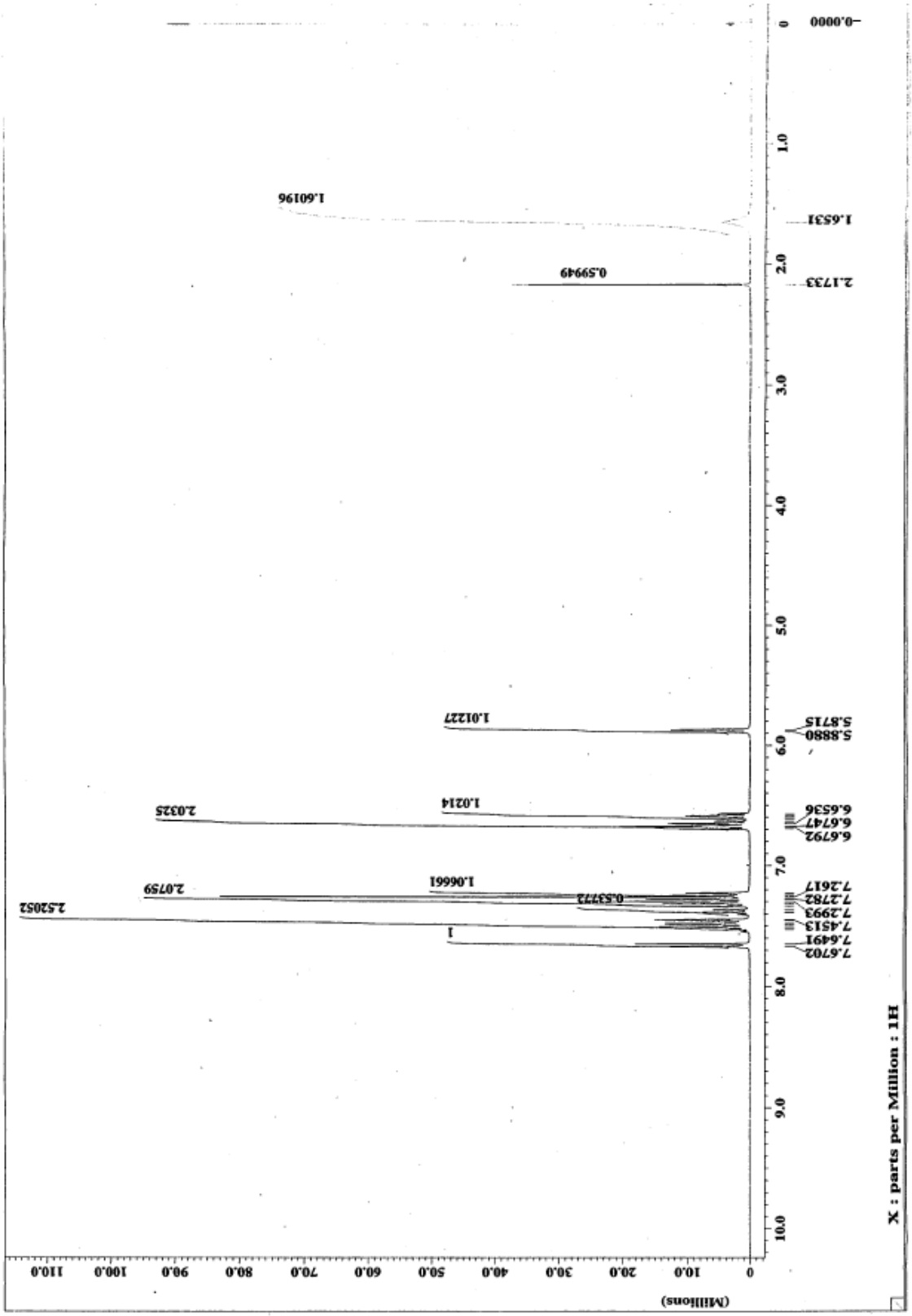
1. ^{1}H NMR spectrum of PXZ-OXD



2. ^{1}H NMR spectrum of 2PXZ-OXD



3. ^{1}H NMR spectrum of PXZ-TAZ



4. ^{1}H NMR spectrum of 2PXZ-TAZ