Supporting Information

Polymorphic mechanoresponsive luminescent material based on fluorene-phenanthroimidazole hybrid by modulation of intramolecular conformation and intermolecular interaction

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1. Synthetic details

Synthesis of 4-(9*H*-fluoren-2-yl)benzaldehyde

Add 2-bromoindole (3.00 g, 12.24 mmol), p-formylbenzeneboronic acid (1.38 g , 9.20 mmol), 1, 1-bis(diphenylphosphino) ferrocene palladium dichloride (0.23 g, 0.31 mmol), potassium carbonate (2.54 g, 18.38 mmol), N, N-dimethylformamide (120 ml) and water (100 ml) to a 500 ml round bottom flask, the temperature was 80 - 95 ℃, and the mixture was stirred under reflux with a nitrogen atmosphere and refluxed for 10 h, cooled to room temperature, and extracted with dichloromethane. A pale white solid was obtained by column chromatography using dichloromethane and n-hexane as eluent. Yield: 2.10 g (64 %). (^{1}H NMR (400MHz $CDCl_3$) δ10.08 (s, 1H), 7.98 (d, J =8.3 Hz 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.79 (d, J =7.8 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.62 (dd, J =13.0, 5.1 Hz, 2H), 7.3 (dd, J =9.9, 4.9Hz, 3H), 3.93 (s, 2H).

Synthesis of 2-(4-(9H-fluoren-2-yl)phenyl)-1-phenyl-1H-phenanthro[9, 10-d]imidazole

9, 10-phenanthrenequinone (0.46 g, 2.40 mmol), aniline (0.86 g, 9.20 mmol), compound 2 (0.55 g, 2.01 mmol) and ammonium acetate (0.62 g, 8.02 mmol) were added to acetic acid (15 mL). After being stirred under a nitrogen atmosphere for 2 h at 120 ℃, the mixture was cooled to room temperature and extracted for 2 or 3 times with dichloromethane. Then the mixture was evaporated under reduced pressure to afford a black solid, which was purified by silica gel column chromatography using dichloromethane/n-hexane (2:1, v/v) as the eluent to afford **PPIF**. Yield: 0.51 g (48 %). ES-MS (m/z) calcd. for $C_{40}H_{26}N_2$, 534.63; found, 535. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.93 (d, J = 8.0 Hz, 1H), 8.74 (dd, J = 24.5, 8.3 Hz, 2H), 7.78 (dt, J = 19.3, 7.4 Hz, 4H), 7.69-7.48 (m, 13H), 7.38 (t, J = 7.4 Hz, 1H), 7.30 (dd, J = 18.3, 7.6 Hz, 3H), 7.19 (d, J = 8.2 Hz, 1H), 3.93 (s, 2H). ^{13}C NMR (151MHz, Chloroform-d) δ 150.52 , 143.93 , 143.50 , 141.78 , 141.34 , 141.29 , 138.79 , 130.23 , 129.89 , 129.78 , 129.37 , 129.18 , 128.36 , 128.18 , 127.35 , 127.01 , 126.85 , 126.83 , 126.29 , 125.87 , 125.73 , 125.05 , 124.96 , 124.13 , 123.63 , 123.10 , 122.97 , 120.88 , 120.14 , 120.02 , 36.98 .

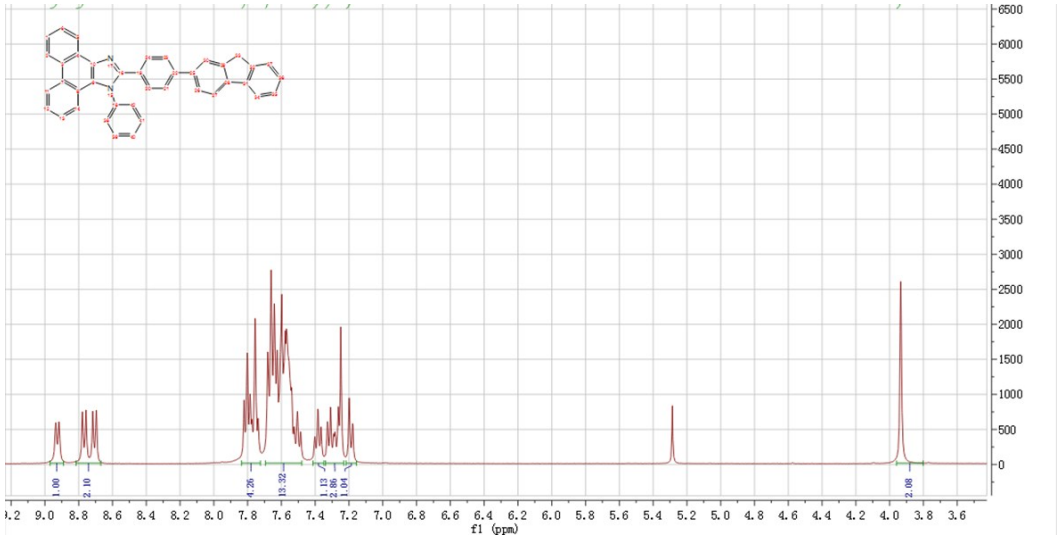

Fig. S1 ^{1}H NMR spectrum of **PPIF.**

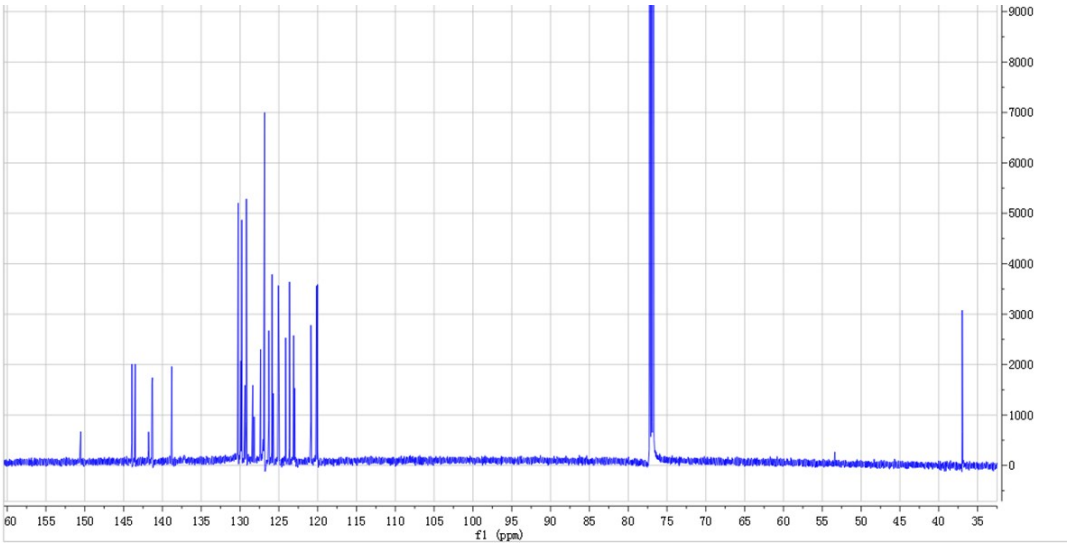

Fig. S2 ^{13}C NMR spectrum of **PPIF**.

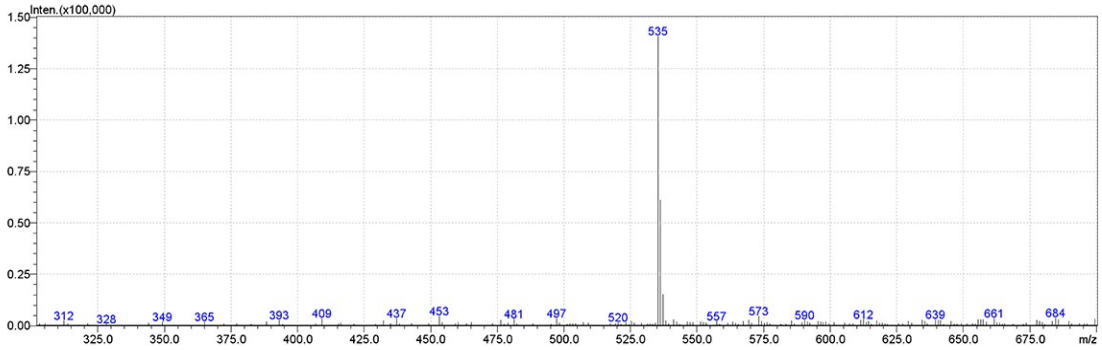

Fig. S3 The MS spectrum of **PPIF**.

2. Single crystal data of PPISF

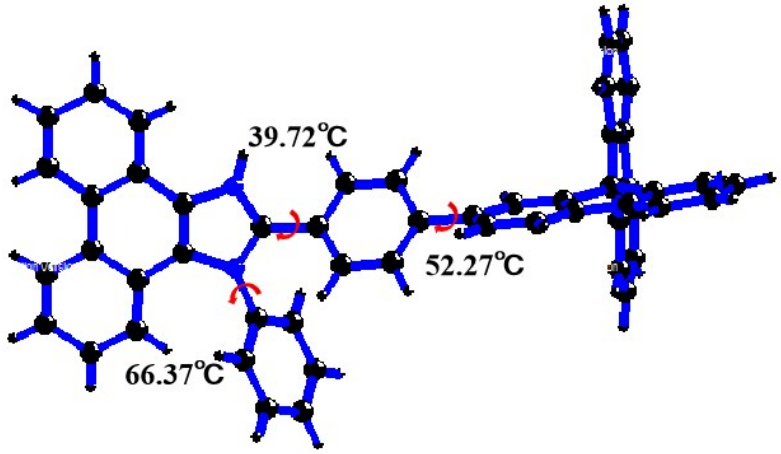

Fig. S4 Crystal structure of **PPISF**.

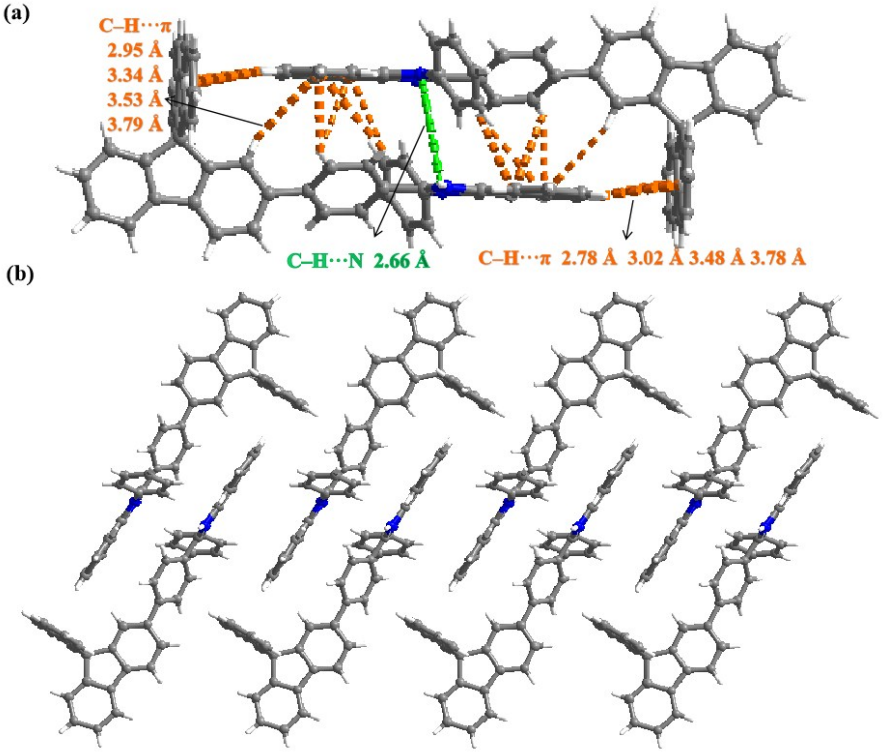

Fig. S5 (a) Molecular interactions and (b) packing modes of **PPISF-T**.

The CCDC number of crystal **PPISF-T** is 1846865, and the space group is P-1. Crystal structure analysis reveals that **PPISF-T** employs a head-to-tail stacking mode and no π-π stacking is formed in neighboring molecules. In **PPISF-T**, the intermolecular C–H···π interactions are mainly concentrated on the phenanthrene ring and neighboring molecularly linked phenyl ring. The interaction distances are 2.95 Å,

3.34 Å, 3.53 Å and 3.79 Å (Fig. S5a). What' s more, C–H···π interaction can be found between spirobifluorene and phenanthrene rings of neighboring molecules. The distances are 2.78, 3.02 , 3.48 and 3.78 Å, respectively In addition, compared with 2.83 Å for **PPIF-M** and 3.18 Å for **PPIF-O** (Fig. 2a and 3a), a stronger C-H···N interaction with an intermolecular distance of 2.66 Å was obtained in **PPISF-T** (Fig. S5b). Therefore, **PPISF-T** shows more C–H···π interactions and stronger C-H···N bonding than those of **PPIF-M** and **PPIF-O**.

Table S1 Crystallographic parameters for **PPISF-T**.

Identification code	**PPISF-T**
Empirical formula	$C_{53}H_{35}Cl_2N_2$
Formula weight	770.73
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.8562(8)
b/Å	13.4286(9)
c/Å	13.4659(5)
α/°	77.628(4)
β/°	86.612(4)
γ/°	68.539(6)
Volume/Å^3	1948.5(2)
Z	2
ρcalcg/cm^3	1.314
μ/mm^{-1}	1.808
F(000)	802.0
Crystal size/mm^3	0.190 × 0.180 × 0.170
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.722 to 131.998
Index ranges	-14 ≤ h ≤ 11, -15 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	11971
Independent reflections	6591 [Rint = 0.1042, Rsigma = 0.1178]
Data/restraints/parameters	6591/0/514
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R1 = 0.1254, wR2 = 0.2505
Final R indexes [all data]	R1 = 0.1832, wR2 = 0.2946
Largest diff. peak/hole / e Å^{-3}	1.03/-0.81

3. Photophysical data and spectra

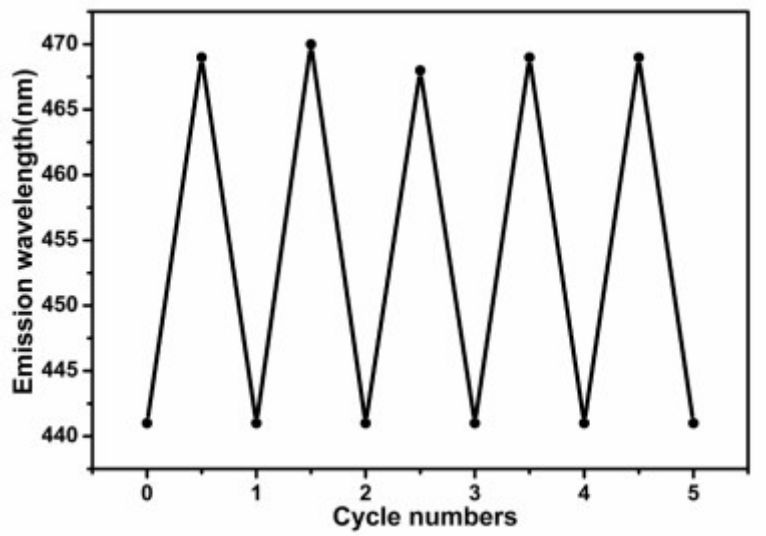

Fig. S6 Emission wavelength of the repeated luminescence switching behavior of grinded **PPIF-M**.

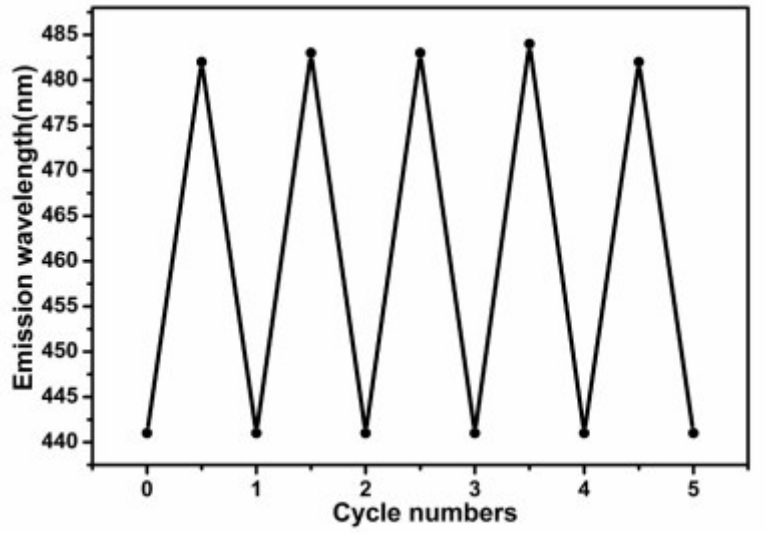

Fig. S7 Emission wavelength of the repeated luminescence switching behavior of grinded **PPIF-O**.

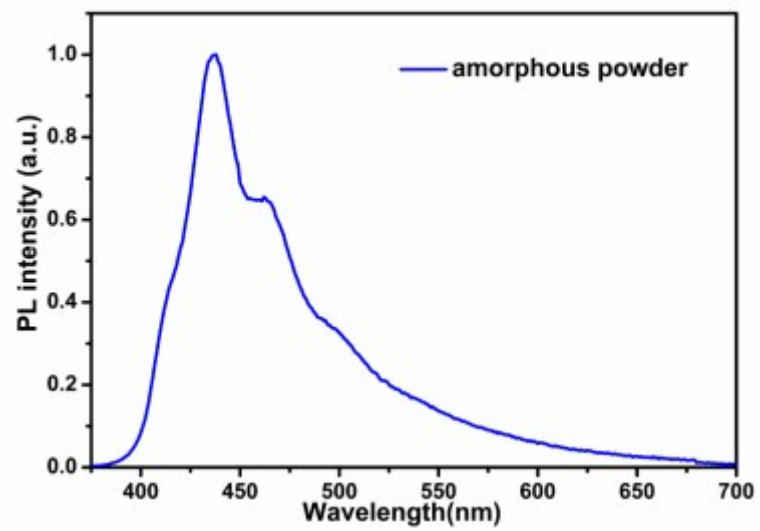

Fig. S8 PL spectra of PPIF in amorphous powders.

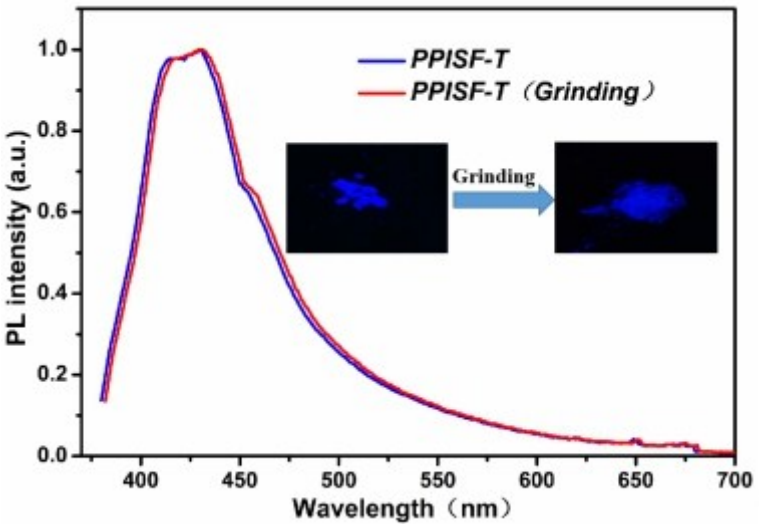

Fig. S9 PL spectra and photos of the crystalline phase transformation upon grinding **PPISF-T** in a mortar under 365 nm UV light.

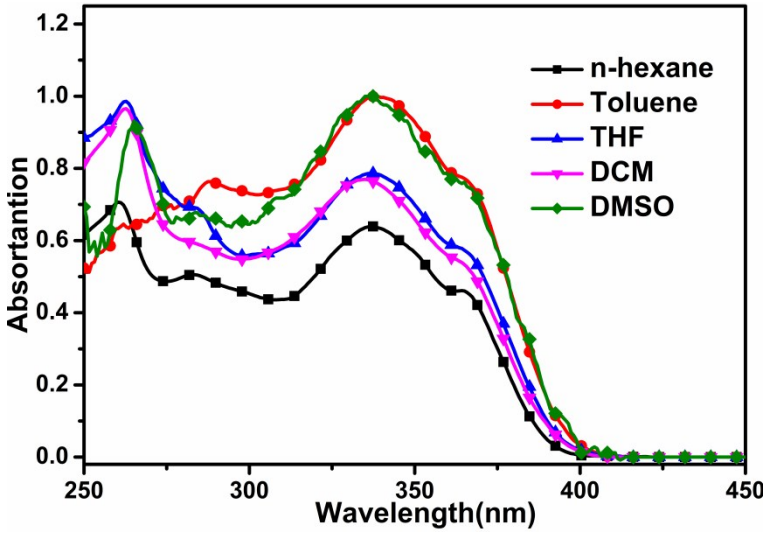

Fig. S10 UV-vis absorption spectra for PPIF in various solutions.

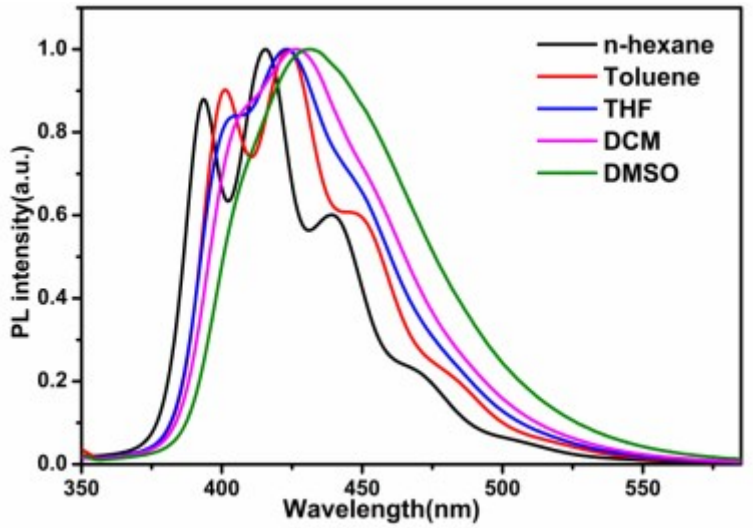

Fig. S11 Emission spectra of PPIF in various solvents with concentration of 1.0×10^{-5} mol L^{-1}.

Table S2 UV absorption, fluorescence emission and fluorescence lifetimes of PPIF in various solvents.

Solvent	λ_{abs} (nm)	λ_{PL} (nm)	□τ(ns)
n-hexane	261,283,337	394 415 439	0.46
toluene	261,287,339	401 424 447	0.45
THF	262 285 338	403 423	0.42
DCM	263,283,335	426	0.43
DMSO	265,286,336	435	0.38

4. Computational details

Table S3 Calculated energies of HOMO, LUMO, S_1 and T_1 orbitals and oscillator strength of transition for **PPIF-M** and **PPIF-O** both for monomer states and their dimer according to their single crystal structures.

Compounds		E_{S1} (ev)	E_{T1} (ev)	ΔE_{ST} (ev)	E_{HOMO} (ev)	E_{LUMO} (ev)	ΔE_g (ev)
PPIF-M	monomer	4.22	3.14	0.68	-5.30	-1.45	3.85
PPIF-O	monomer	4.06	3.18	0.88	-5.09	-1.34	3.75

* For dimer, the transition from S_0 to S_1 was corresponding to intermolecular charge transfer absorption,the other from S_0 to S_2 was corresponding to intramolecular charge transfer absorption.

5. Single crystal data of PPIF-M and PPIF-O

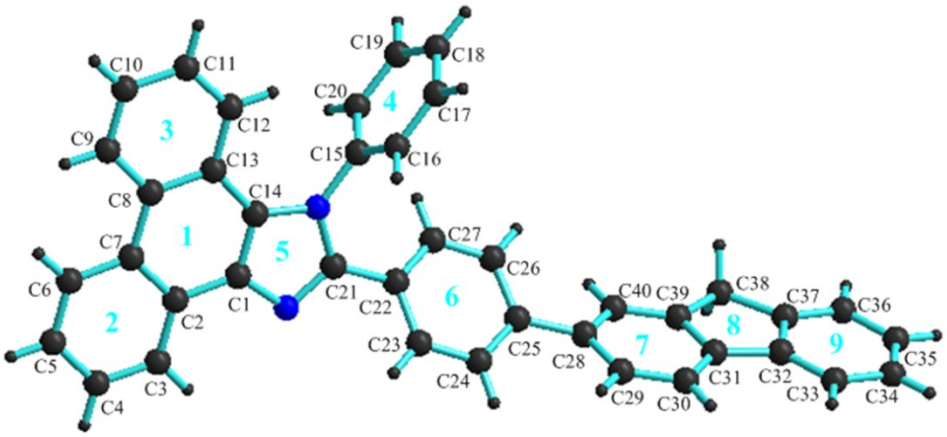

Fig. S12 Single crystal structure for **PPIF-M**.

TableS4 Details of C-H···π interactions for **PPIF-M**.

C-H(I)···π(J)	$D_{H\cdots\pi}$(Å)	$D_{H\text{-}Per}$(Å)	Gamma(º)	AC-H-π (º)	$D_{C\cdots\pi}$ (Å)	$A_{C\text{-}H,\pi}$ (º)
C-H(19)···π(2)	2.78	2.72	12.37	148.7	3.62	29.03
C-H(20)···π(2)	3.71	2.76	41.98	106.59	4.00	31.57
C-H(36)···π(3)	3.07	3.05	6.36	149.78	3.92	23.88
C-H(38A)···π(3)	3.88	2.93	40.94	95.95	4.01	68.13
C-H(38B)···π(1)	2.90	2.05	44.87	156.83	3.83	40.99
C-H(38B)···π(3)	3.58	3.12	29.23	115.6	4.01	40.99

* [π(J)] = Center of gravity of ring J (Plane number below); [H-Perp] = Perpendicular distance of H to ring plane J; [Gamma] = Angle between π-H vector and ring J normal; [C-H···π] = C-H-π angle (degrees); [C···π] = Distance of X to Cg (Angstrom); [C-H, π] = Angle of the C-H bond with the Pi-plane (i.e.' Perpendicular = 90 degrees, Parallel = 0 degrees)

Table S5 Details of C-H···N interactions for **PPIF-M**.

N(k)-H(L)	$D_{N\text{-}H}$(Å)	$D_{N\text{-}C}$(Å)
N(2)-H(38A)-C(38)	3.35	3.50
N(1)-H(38B)-C(38)	3.48	3.50
N(2)-H(38B)-C(38)	2.86	4.35
N(1)-H(40)-C(40)	3.39	4.03
N(2)-H(40)-C(40)	3.33	4.46

Table S6 Bond distances (Å) for **PPIF-M**.

Atom	Atom	Length/Å	Atom	Atom	Atom	Length/Å
N1	C21	1.390(2)		C18	C19	1.380(3)
N1	C14	1.395(2)		C19	C20	1.385(3)

N1	C15	1.438(2)	C21	C22	1.471(2)
N2	C21	1.319(2)	C22	C23	1.395(2)
N2	C1	1.374(2)	C22	C27	1.396(2)
C1	C14	1.380(2)	C23	C24	1.388(2)
C1	C2	1.436(2)	C24	C25	1.394(2)
C2	C3	1.399(2)	C25	C26	1.399(2)
C2	C7	1.417(2)	C25	C28	1.488(2)
C3	C4	1.379(2)	C26	C27	1.385(2)
C4	C5	1.394(2)	C28	C40	1.399(2)
C5	C6	1.374(3)	C28	C29	1.402(2)
C6	C7	1.410(2)	C29	C30	1.391(2)
C7	C8	1.469(2)	C30	C31	1.385(2)
C8	C9	1.412(2)	C31	C39	1.397(2)
C8	C13	1.426(2)	C31	C32	1.468(2)
C9	C10	1.374(3)	C32	C33	1.387(2)
C10	C11	1.395(3)	C32	C37	1.399(2)
C11	C12	1.378(2)	C33	C34	1.383(2)
C12	C13	1.411(2)	C34	C35	1.390(2)
C13	C14	1.440(2)	C35	C36	1.391(3)
C15	C20	1.384(2)	C36	C37	1.388(2)
C15	C16	1.390(2)	C37	C38	1.511(2)
C16	C17	1.382(2)	C38	C39	1.510(2)
C17	C18	1.389(3)	C39	C40	1.386(2)

Table S7 Bond angles for **PPIF-M**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C21	N1	C14	106.26(13)	C15	C20	C19	119.34(16)
C21	N1	C15	126.74(13)	N2	C21	N1	111.98(13)
C14	N1	C15	126.90(13)	N2	C21	C22	122.99(14)
C21	N2	C1	105.23(13)	N1	C21	C22	124.94(14)
N2	C1	C14	111.56(14)	C23	C22	C27	118.28(14)
N2	C1	C2	126.51(15)	C23	C22	C21	117.25(14)
C14	C1	C2	121.85(14)	C27	C22	C21	124.47(14)
C3	C2	C7	121.03(15)	C24	C23	C22	120.78(15)
C3	C2	C1	121.64(15)	C23	C24	C25	121.23(15)
C7	C2	C1	117.32(15)	C24	C25	C26	117.58(14)
C4	C3	C2	120.05(16)	C24	C25	C28	121.81(14)
C3	C4	C5	119.68(16)	C26	C25	C28	120.41(14)
C6	C5	C4	120.91(16)	C27	C26	C25	121.41(15)
C5	C6	C7	121.20(16)	C26	C27	C22	120.57(14)

C6	C7	C2	117.13(15)	C40	C28	C29	118.64(14)
C6	C7	C8	122.44(15)	C40	C28	C25	121.23(14)
C2	C7	C8	120.42(14)	C29	C28	C25	119.90(14)
C9	C8	C13	117.71(16)	C30	C29	C28	121.60(14)
C9	C8	C7	120.99(15)	C31	C30	C29	118.88(14)
C13	C8	C7	121.30(14)	C30	C31	C39	120.30(15)
C10	C9	C8	121.81(17)	C30	C31	C32	130.83(14)
C9	C10	C11	120.11(16)	C39	C31	C32	108.86(13)
C12	C11	C10	120.11(17)	C33	C32	C37	120.62(15)
C11	C12	C13	120.82(17)	C33	C32	C31	130.92(14)
C12	C13	C8	119.41(15)	C37	C32	C31	108.45(14)
C12	C13	C14	124.81(15)	C34	C33	C32	119.11(15)
C8	C13	C14	115.78(14)	C33	C34	C35	120.22(16)
C1	C14	N1	104.96(13)	C34	C35	C36	121.23(16)
C1	C14	C13	123.25(14)	C37	C36	C35	118.47(16)
N1	C14	C13	131.77(14)	C36	C37	C32	120.36(16)
C20	C15	C16	120.80(15)	C36	C37	C38	129.65(15)
C20	C15	N1	119.33(14)	C32	C37	C38	109.95(14)
C16	C15	N1	119.87(14)	C39	C38	C37	102.86(13)
C17	C16	C15	119.16(16)	C40	C39	C31	120.68(14)
C16	C17	C18	120.44(17)	C40	C39	C38	129.48(15)
C19	C18	C17	119.77(17)	C31	C39	C38	109.84(14)
C18	C19	C20	120.46(16)	C39	C40	C28	119.84(14)

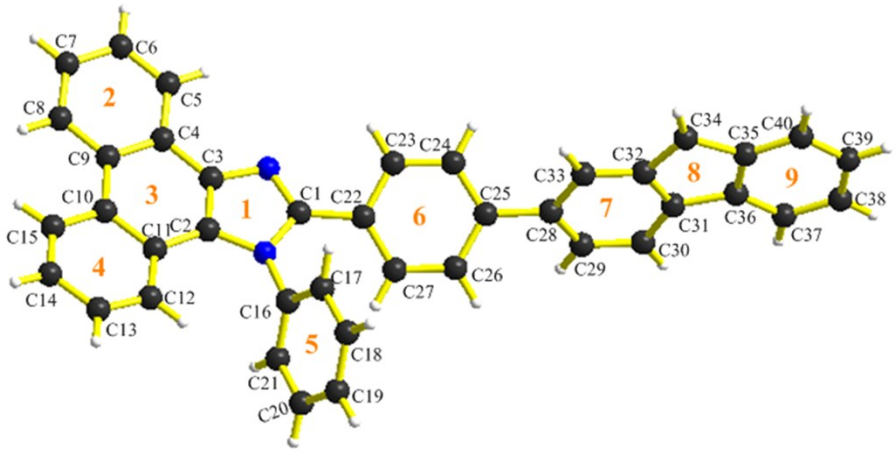

Fig. S13 Single crystal structure for **PPIF-O**.

Table S8 Details of C-H···π interactions for **PPIF-O**.

C-H(I)···π(J)	$D_{H\cdots\pi}$(Å)	$D_{H\text{-}Perp}$(Å)	Gamma(º)	$A_{C\text{-}H\text{-}\pi}$ (º)	$D_{C\cdots\pi}$ (Å)	$A_{C\text{-}H,\pi}$ (º)
C-H(33)···π(9)	3.77	3.25	30.52	143.97	3.77	38.89
C-H(34)···π(7)	2.56	2.53	8.17	142.64	2.56	27.47
C-H(40)···π(6)	3.03	2.90	16.68	137.42	3.03	42.74

* [π(J)] = Center of gravity of ring J (Plane number below); [H-Perp] = Perpendicular distance of H to ring plane J; [Gamma] = Angle between π-H vector and ring J normal; [C-H···π] = C-H-π angle (degrees); [C···π] = Distance of X to Cg (Angstrom); [C-H, π] = Angle of the C-H bond with the Pi-plane (i.e.' Perpendicular = 90 degrees, Parallel = 0 degrees).

Table S9 Details of C-H···N interactions for **PPIF-O**.

N(k)-H(L)	$D_{N\text{-}H}$(Å)	$D_{N\text{-}C}$(Å)
N(2)-H(19)-C(19)	3.18	3.88
N(2)-H(20)-C(20)	3.99	4.21
N(2)-H(21)-C(21)	3.75	4.18

Table S10 Bond distances (Å) for **PPIF-O**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
N1	C1	1.394(7)	N3	C41	1.381(7)
N1	C15	1.380(7)	N3	C55	1.401(8)
N1	C35	1.458(8)	N3	C75	1.419(8)
N2	C14	1.379(8)	N4	C54	1.401(8)
N2	C15	1.316(8)	N4	C55	1.319(8)
C1	C2	1.440(8)	C41	C42	1.441(8)
C1	C14	1.362(9)	C41	C54	1.374(9)
C2	C3	1.382(9)	C42	C43	1.417(9)
C2	C7	1.437(9)	C42	C47	1.423(9)
C3	C4	1.374(9)	C43	C44	1.365(9)
C4	C5	1.382(10)	C44	C45	1.383(10)
C5	C6	1.376(10)	C45	C46	1.359(9)
C6	C7	1.411(9)	C46	C47	1.400(8)
C7	C8	1.457(9)	C47	C48	1.478(9)
C8	C9	1.419(10)	C48	C49	1.390(10)
C8	C13	1.405(8)	C48	C53	1.411(9)
C9	C10	1.367(10)	C49	C50	1.366(10)
C10	C11	1.381(10)	C50	C51	1.401(10)
C11	C12	1.372(10)	C51	C52	1.367(10)
C12	C13	1.391(9)	C52	C53	1.383(10)

C13	C14	1.439(9)	C53	C54	1.434(9)
C15	C16	1.466(8)	C55	C56	1.459(8)
C16	C17	1.376(9)	C56	C57	1.387(9)
C16	C21	1.383(9)	C56	C61	1.374(9)
C17	C18	1.376(8)	C57	C58	1.382(8)
C18	C19	1.379(8)	C58	C59	1.394(8)
C19	C20	1.372(9)	C59	C60	1.393(8)
C19	C22	1.496(8)	C59	C62	1.491(8)
C20	C21	1.379(9)	C60	C61	1.392(8)
C22	C23	1.388(8)	C62	C63	1.395(8)
C22	C34	1.399(8)	C62	C67	1.377(8)
C23	C24	1.385(8)	C63	C64	1.385(8)
C24	C25	1.384(8)	C64	C65	1.384(8)
C25	C26	1.478(8)	C65	C66	1.375(8)
C25	C33	1.404(8)	C65	C70	1.479(8)
C26	C27	1.370(9)	C66	C67	1.377(8)
C26	C31	1.402(8)	C66	C68	1.489(8)
C27	C28	1.384(9)	C68	C69	1.520(8)
C28	C29	1.377(11)	C69	C70	1.377(9)
C29	C30	1.376(11)	C69	C74	1.369(8)
C30	C31	1.388(9)	C70	C71	1.394(9)
C31	C32	1.493(9)	C71	C72	1.414(9)
C32	C33	1.492(8)	C72	C73	1.363(11)
C33	C34	1.388(8)	C73	C74	1.372(10)
C35	C36	1.357(9)	C75	C76	1.375(9)
C35	C40	1.365(8)	C75	C80	1.396(8)
C36	C37	1.385(10)	C76	C77	1.351(10)
C37	C38	1.376(10)	C77	C78	1.359(11)
C38	C39	1.366(12)	C78	C79	1.373(13)
C39	C40	1.378(11)	C79	C80	1.377(10)

Table S11 Bond angles for **PPIF-O**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C1	N1	C35	128.2(5)	C41	N3	C55	106.7(5)
C15	N1	C1	106.5(5)	C41	N3	C75	129.1(5)
C15	N1	C35	124.4(5)	C55	N3	C75	123.3(5)
C15	N2	C14	105.0(5)	C55	N4	C54	104.6(5)
N1	C1	C2	130.7(6)	N3	C41	C42	132.4(6)
C14	C1	N1	105.0(5)	C54	C41	N3	105.6(5)
C14	C1	C2	124.0(6)	C54	C41	C42	121.8(6)

C3	C2	C1	126.2(6)	C43	C42	C41	124.6(6)
C3	C2	C7	119.3(6)	C43	C42	C47	119.0(6)
C7	C2	C1	114.4(6)	C47	C42	C41	116.3(6)
C4	C3	C2	122.6(7)	C44	C43	C42	121.1(6)
C3	C4	C5	119.1(7)	C43	C44	C45	119.8(7)
C6	C5	C4	120.0(7)	C46	C45	C44	120.2(6)
C5	C6	C7	122.6(7)	C45	C46	C47	122.8(6)
C2	C7	C8	122.1(6)	C42	C47	C48	121.1(5)
C6	C7	C2	116.2(6)	C46	C47	C42	117.0(6)
C6	C7	C8	121.5(6)	C46	C47	C48	121.7(6)
C9	C8	C7	122.6(6)	C49	C48	C47	122.0(6)
C13	C8	C7	120.1(6)	C49	C48	C53	117.4(6)
C13	C8	C9	117.1(6)	C53	C48	C47	120.5(6)
C10	C9	C8	120.8(7)	C50	C49	C48	121.1(7)
C9	C10	C11	121.6(7)	C49	C50	C51	121.4(7)
C12	C11	C10	118.8(7)	C52	C51	C50	118.0(7)
C11	C12	C13	121.3(7)	C51	C52	C53	121.4(7)
C8	C13	C14	117.6(6)	C48	C53	C54	116.4(6)
C12	C13	C8	120.5(6)	C52	C53	C48	120.6(6)
C12	C13	C14	121.7(6)	C52	C53	C54	122.8(6)
N2	C14	C13	126.6(6)	N4	C54	C53	124.9(6)
C1	C14	N2	111.7(5)	C41	C54	N4	111.3(5)
C1	C14	C13	121.7(6)	C41	C54	C53	123.7(6)
N1	C15	C16	125.2(5)	N3	C55	C56	125.7(5)
N2	C15	N1	111.9(5)	N4	C55	N3	111.8(5)
N2	C15	C16	122.8(5)	N4	C55	C56	122.3(6)
C17	C16	C15	126.5(5)	C57	C56	C55	125.8(6)
C17	C16	C21	117.3(6)	C61	C56	C55	117.0(6)
C21	C16	C15	115.9(5)	C61	C56	C57	117.2(6)
C18	C17	C16	122.0(6)	C58	C57	C56	121.1(6)
C17	C18	C19	120.2(6)	C57	C58	C59	122.6(6)
C18	C19	C22	121.1(5)	C58	C59	C62	123.2(5)
C20	C19	C18	118.3(6)	C60	C59	C58	115.3(5)
C20	C19	C22	120.6(5)	C60	C59	C62	121.4(5)
C19	C20	C21	121.4(6)	C59	C60	C61	122.1(6)
C20	C21	C16	120.5(6)	C56	C61	C60	121.6(6)
C23	C22	C19	122.3(5)	C63	C62	C59	120.8(5)
C23	C22	C34	118.0(5)	C67	C62	C59	120.9(5)
C34	C22	C19	119.7(5)	C67	C62	C63	118.2(5)
C24	C23	C22	123.2(6)	C64	C63	C62	121.7(5)

C25	C24	C23	118.3(5)	C65	C64	C63	118.5(5)
C24	C25	C26	131.0(5)	C64	C65	C70	130.9(5)
C24	C25	C33	119.9(5)	C66	C65	C64	120.3(5)
C33	C25	C26	109.1(5)	C66	C65	C70	108.8(5)
C27	C26	C25	131.8(5)	C65	C66	C67	120.7(5)
C27	C26	C31	121.0(6)	C65	C66	C68	110.0(5)
C31	C26	C25	107.1(5)	C67	C66	C68	129.3(5)
C26	C27	C28	119.6(6)	C62	C67	C66	120.6(5)
C29	C28	C27	119.5(7)	C66	C68	C69	103.4(5)
C30	C29	C28	121.6(7)	C70	C69	C68	109.1(5)
C29	C30	C31	119.2(7)	C74	C69	C68	129.3(6)
C26	C31	C32	110.6(5)	C74	C69	C70	121.3(6)
C30	C31	C26	119.0(6)	C69	C70	C65	108.6(5)
C30	C31	C32	130.4(6)	C69	C70	C71	121.2(6)
C33	C32	C31	103.8(5)	C71	C70	C65	130.2(6)
C25	C33	C32	109.3(5)	C70	C71	C72	115.8(7)
C34	C33	C25	120.8(5)	C73	C72	C71	122.0(7)
C34	C33	C32	129.9(5)	C72	C73	C74	120.6(6)
C33	C34	C22	119.8(5)	C69	C74	C73	118.8(7)
C36	C35	N1	120.4(5)	C76	C75	N3	121.9(5)
C36	C35	C40	121.7(6)	C76	C75	C80	118.4(6)
C40	C35	N1	117.9(6)	C80	C75	N3	119.7(5)
C35	C36	C37	119.4(6)	C77	C76	C75	121.4(7)
C38	C37	C36	119.9(7)	C76	C77	C78	120.5(7)
C39	C38	C37	119.1(7)	C77	C78	C79	119.8(7)
C38	C39	C40	121.5(7)	C78	C79	C80	120.2(7)
C35	C40	C39	118.3(7)	C79	C80	C75	119.6(7)

Table S12 Bond distances (Å) for **PPISF-T**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N3	C21	1.370(6)	C15	C16	1.382(8)
N3	C14	1.406(6)	C29	C30	1.394(7)
N3	C15	1.441(6)	C13	C12	1.410(7)
N6	C21	1.336(6)	C13	C14	1.434(6)
N6	C1	1.391(6)	C7	C6	1.409(7)
C33	C28	1.388(8)	C7	C2	1.419(7)
C33	C32	1.393(6)	C22	C27	1.391(7)
C1	C14	1.359(6)	C2	C3	1.395(7)
C1	C2	1.431(6)	C34	C35	1.383(7)
C41	C42	1.345(7)	C34	C39	1.428(8)

C41	C40	1.402(6)	C6	C5	1.361(7)
C51	C50	1.355(7)	C3	C4	1.377(7)
C51	C46	1.426(8)	C46	C47	1.411(8)
C51	C52	1.563(7)	C27	C26	1.403(6)
C28	C29	1.401(8)	C11	C12	1.364(7)
C28	C25	1.493(6)	C11	C10	1.397(7)
C8	C9	1.390(7)	C44	C43	1.388(8)
C8	C13	1.427(6)	C43	C42	1.407(9)
C8	C7	1.472(6)	C10	C9	1.362(7)
C23	C22	1.362(7)	C35	C36	1.388(8)
C23	C24	1.380(7)	C39	C38	1.369(7)
C52	C40	1.478(7)	C4	C5	1.414(8)
C52	C32	1.514(8)	C20	C19	1.404(7)
C52	C39	1.532(6)	C47	C48	1.354(8)
C45	C44	1.361(7)	C17	C18	1.382(9)
C45	C40	1.431(8)	C17	C16	1.413(7)
C45	C46	1.465(6)	C37	C38	1.387(8)
C25	C24	1.381(7)	C37	C36	1.413(10)
C25	C26	1.390(7)	C50	C49	1.426(9)
C31	C30	1.373(9)	C48	C49	1.402(10)
C31	C32	1.415(8)	C19	C18	1.378(9)
C31	C34	1.470(6)	C11	C53	1.660(9)
C21	C22	1.484(6)	C12	C53	1.661(10)
C15	C20	1.376(8)			

Table S13 Bond angles for **PPISF-T**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C21	N3	C14	106.8(4)	C3	C2	C7	120.8(4)
C21	N3	C15	124.3(4)	C3	C2	C1	122.8(4)
C14	N3	C15	128.8(4)	C7	C2	C1	116.2(4)
C21	N6	C1	104.7(4)	C33	C32	C31	119.7(5)
C28	C33	C32	119.9(5)	C33	C32	C52	128.8(5)
C14	C1	N6	111.4(4)	C31	C32	C52	111.5(4)
C14	C1	C2	122.9(4)	C41	C40	C45	118.4(5)
N6	C1	C2	125.6(4)	C41	C40	C52	128.4(5)
C42	C41	C40	120.7(5)	C45	C40	C52	113.1(4)
C50	C51	C46	123.0(6)	C35	C34	C39	120.2(5)
C50	C51	C52	129.0(6)	C35	C34	C31	130.7(6)
C46	C51	C52	108.0(4)	C39	C34	C31	109.1(4)
C33	C28	C29	119.5(4)	C5	C6	C7	122.2(5)

C33	C28	C25	121.7(5)	C1	C14	N3	105.3(4)
C29	C28	C25	118.8(5)	C1	C14	C13	123.4(4)
C9	C8	C13	117.8(4)	N3	C14	C13	131.3(4)
C9	C8	C7	121.6(4)	C4	C3	C2	121.3(5)
C13	C8	C7	120.5(4)	C47	C46	C51	118.9(5)
C22	C23	C24	121.1(5)	C47	C46	C45	130.4(5)
C40	C52	C32	115.3(4)	C51	C46	C45	110.7(5)
C40	C52	C39	110.3(4)	C22	C27	C26	119.2(4)
C32	C52	C39	102.0(4)	C12	C11	C10	120.1(5)
C40	C52	C51	102.0(4)	C25	C26	C27	120.4(5)
C32	C52	C51	113.1(4)	C45	C44	C43	120.3(6)
C39	C52	C51	114.7(4)	C44	C43	C42	119.7(5)
C44	C45	C40	120.1(5)	C9	C10	C11	119.3(4)
C44	C45	C46	133.8(6)	C34	C35	C36	119.4(6)
C40	C45	C46	106.1(4)	C38	C39	C34	120.0(5)
C24	C25	C26	118.9(4)	C38	C39	C52	130.3(6)
C24	C25	C28	120.1(4)	C34	C39	C52	109.5(4)
C26	C25	C28	120.9(4)	C31	C30	C29	119.0(5)
C30	C31	C32	120.8(4)	C10	C9	C8	122.9(5)
C30	C31	C34	131.5(5)	C11	C12	C13	121.4(5)
C32	C31	C34	107.7(5)	C3	C4	C5	118.1(5)
N6	C21	N3	111.7(4)	C23	C24	C25	120.5(5)
N6	C21	C22	122.4(4)	C15	C20	C19	119.4(5)
N3	C21	C22	125.9(4)	C41	C42	C43	120.8(5)
C20	C15	C16	121.3(4)	C48	C47	C46	118.3(6)
C20	C15	N3	119.2(5)	C18	C17	C16	118.8(6)
C16	C15	N3	119.3(5)	C38	C37	C36	120.2(5)
C30	C29	C28	121.3(6)	C15	C16	C17	119.4(6)
C12	C13	C8	118.3(4)	C39	C38	C37	120.0(6)
C12	C13	C14	125.5(4)	C51	C50	C49	117.1(6)
C8	C13	C14	115.9(4)	C6	C5	C4	120.8(5)
C6	C7	C2	116.4(4)	C35	C36	C37	120.2(5)
C6	C7	C8	122.6(4)	C47	C48	C49	122.8(6)
C2	C7	C8	120.9(4)	C18	C19	C20	119.6(6)
C23	C22	C27	119.9(4)	C48	C49	C50	119.9(5)
C23	C22	C21	121.7(5)	C19	C18	C17	121.4(5)
C27	C22	C21	118.3(4)	C11	C53	C12	121.8(6)