Supporting Information

Photoinduced Enhancement of Intraligand Charge-Transfer of a Crystalline 3,3'-diindolyl(3-pyridyl)methane

Chaowat Kaenpracha, [a] Praewpan Katrun, [b] Kittipong Chainok, [c] Chattarika Sukpattanacharoen,[d] Nawee Kungwan,[d] and Jaursup Boonmak [a,*]

[a]*Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand.(e-mail: jaursup@kku.ac.th)*
[b]*Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand*
[c] *Thammasat University Research Unit in Multifunctional Crystalline Materials and Applications (TU-MCMA), Faculty of Science and Technology, Thammasat University, Pathum Thani 12121, Thailand*
[d] *Department of Chemistry, Faculty of Science, Chiang Mai University, Muang District, Chiang Mai 50200, Thailand*

*E-mail: jaursup@kku.ac.th

Tables S1-S16

Table S1 Crystal data and structural refinement for **PMDI·MeOH** and **PMDI·MeOH´** (CCDC nos. 2266873-2266874).

crystal data	**PMDI·MeOH**	**PMDI·MeOH´**
formula	$C_{23}H_{21}N_3O$	$C_{23}H_{21}N_3O$
formula weight	355.443	355.443
temperature (K)	296.15	296.15
crystal system	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/n$
***a* (Å)**	14.5200(7)	14.5277(5)
***b* (Å)**	9.3992(5)	9.4021(4)
***c* (Å)**	15.1096(8)	15.0821(6)
α (°)	90	90
β (°)	112.583(2)	112.559(1)
γ (°)	90	90
***V* (Å^3)**	1903.99(17)	1902.45(13)
Z	4	4
D_{calc} (g cm^{-3})	1.240	1.241
***F*(000)**	752.442	752.442
μ (Mo Kα) (mm^{-1})	0.077	0.078
data collected	3602	4533
unique data (R_{int})	2805(0.0912)	3596(0.0968)
R_1[a]/ wR_2[b] [$I > 2\sigma(I)$]	0.0694/0.1599	0.0746/0.1557
R_1[a]/ wR_2[b] (all data)	0.0923/0.1730	0.0964/0.1672
GOF	1.0789	1.0891
max/min e$^-$ density (e Å^{-3})	0.3424/-0.3314	0.2700/-0.3204

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR_2 = \{\sum[w(|F_0| - |F_c|)]^2 /\sum[w|F_0|^2]\}^{1/2}$.

Table S2 Selected bond distances (Å) of **PMDI·MeOH** and **PMDI·MeOH´.**

Bond angles	**PMDI·MeOH**	**PMDI·MeOH´**
O(1) – C(1)	1.415(5)	1.409(5)
N(1) – C(2)	1.342(4)	1.339(3)
N(1) – C(6)	1.333(4)	1.331(3)
N(2) – C(8)	1.376(3)	1.377(3)
N(2) – C(15)	1.373(4)	1.370(3)
N(3) – C(16)	1.373(4)	1.376(3)
N(3) – C(23)	1.378(4)	1.373(3)
C(7) – C(9)	1.514(3)	1.511(3)
C(7) – C(17)	1.505(4)	1.505(3)

Table S3 Selected bond angles (°) of **PMDI·MeOH** and **PMDI·MeOH´.**

Bond angles	**PMDI·MeOH**	**PMDI·MeOH´**
C(2) – N(1) – C(6)	116.9(3)	117.1(2)
C(8) – N(2) – C(15)	108.8(2)	108.86(18)
C(16) – N(3) – C(23)	108.7(2)	108.8(2)
C(3) – N(7) – C(9)	111.2(2)	111.30(17)
C(3) – N(7) – C(17)	112.2(2)	112.31(17)
C(9) – N(7) – C(17)	114.71(19)	114.68(17)

Table S4 Hydrogen bond lengths (Å) and angles (°) for **PMDI·MeOH** and **PMDI·MeOH´**.

PMDI·MeOH/ PMDI·MeOH´				
D-H···A	**d(D-H)**/Å	**d(H···A)**/Å	**d(D···A)**/Å	**<(DHA)**/°
O(1)−H···N(1)	0.82(2)/0.82(2)	1.95(3)/(1.93(2)	2.715(3)/(2.716(3)	156(3)/161(2)
N(2)−H···O(1)	0.860(3)/0.860(3)	2.180(3)/2.180(3)	3.000(3)/3.000(3)	159.3(3)/159.3(3)
N(3)−H···O(1)	0.860(3)/0.860(3)	2.307(3)/2.310(3)	2.993(3)/2.993(3)	136.8(3)/136.6(2)

Table S5 π-interactions distances (Å) for **PMDI·MeOH** and **PMDI·MeOH´**.

PMDI·MeOH/ PMDI·MeOH´		
π-interaction	**d(H···cg)**/Å	**<(C-H···cg)**/°
C(4) − H···cg(5)	2.628(3)/2.630(2)	141.5(3)/141.2(3)
C(5) − H···cg(1)	2.985(3)/2.987(3)	139.7(3)/139.9(3)
C(6) − H···cg(4)	2.986(3)/2.986(3)	140.0(3)/140.5(3)
C(8) − H···cg(2)	2.854(3)/2.853(2)	125.0(3)/125.1(2)
C(14) − H ···cg(4)	3.710(3)/3.708(2)	77.1(3)/77.3(2)

Table S6 Crystal data and structural refinement for the same single crystal of **PMDI·MeOH** at various UV irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks (CCDC nos. 2303197-2303201).

crystal data	As-prepared	25 min	40 min	80 min	2 weeks
formula	$C_{23}H_{21}N_3O$	$C_{23}H_{21}N_3O$	$C_{23}H_{21}N_3O$	$C_{23}H_{21}N_3O$	$C_{23}H_{21}N_3O$
formula weight	355.443	355.443	355.443	355.443	355.443
temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
***a* (Å)**	14.5114(18)	14.4915(18)	14.4807(19)	14.4831(18)	14.4804(19)
***b* (Å)**	9.3994(11)	9.3952(9)	9.3916(10)	9.3913(9)	9.3873(10)
***c* (Å)**	15.0586(18)	15.0402(19)	15.0389(19)	15.0356(19)	15.0373(19)
α (°)	90	90	90	90	90
β (°)	112.506(4)	112.575(4)	112.567(4)	112.580(4)	112.596(4)
γ (°)	90	90	90	90	90
***V* (Å^3)**	1897.5(4)	1890.8(4)	1888.6(4)	1888.3(4)	1887.1(4)
Z	4	4	4	4	4
D_{calc} (g cm^{-3})	1.244	1.249	1.250	1.250	1.251
***F*(000)**	752.442	752.442	752.442	752.442	752
μ (Mo Kα) (mm^{-1})	0.078	0.078	0.078	0.078	0.078
data collected	3592	3727	3720	3720	3448
unique data (R_{int})	2222(0.0560)	2056(0.0650)	2036(0.0665)	2049 (0.0657)	2145(0.0452)
R_1[a]/ wR_2[b] [$I > 2\sigma(I)$]	0.1083/0.2779	0.1197/0.3027	0.1119/0.2865	0.1189/0.3019	0.1228/0.3134
R_1[a]/ wR_2[b] (all data)	0.1548/0.4118	0.1787/0.4518	0.1730/0.4333	0.1776/0.4517	0.1708/0.4094
GOF	1.5726	1.6254	1.5304	1.6190	1.5692
max/min e$^-$ density (e Å^{-3})	0.5477/-0.4368	0.5526/-0.4247	0.4400/-0.4421	0.5611/-0.5150	0.5626/-0.4913

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR_2 = \{\sum[w(|F_0| - |F_c|)]^2 /\sum[w|F_0|^2]\}^{1/2}$.

Table S7 Selected bond distances (Å) for the same single crystal of **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

Bond angles	As-prepared	25 min	40 min	80 min	2 weeks
O(1) – C(1)	1.408(8)	1.408(9)	1.409(9)	1.408(9)	1.394(9)
N(1) – C(2)	1.342(6)	1.332(8)	1.335(8)	1.341(8)	1.343(8)
N(1) – C(6)	1.334(7)	1.333(8)	1.335(7)	1.330(7)	1.337(7)
N(2) – C(8)	1.374(5)	1.376(7)	1.378(6)	1.373(7)	1.377(6)
N(2) – C(11)	1.366(6)	1.371(6)	1.367(6)	1.365(7)	1.365(6)
N(3) – C(16)	1.379(7)	1.379(8)	1.376(8)	1.380(8)	1.380(8)
N(3) – C(19)	1.363(6)	1.371(7)	1.369(7)	1.365(7)	1.370(6)
C(7) – C(9)	1.505(6)	1.507(6)	1.510(6)	1.501(6)	1.502(6)
C(7) – C(17)	1.508(6)	1.490(8)	1.489(6)	1.493(7)	1.492(6)

Table S8 Selected bond angles (°) for the same single crystal of **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

Bond angles	As-prepared	25 min	40 min	80 min	2 weeks
C(2) – N(1) – C(6)	117.2(4)	117.8(5)	117.0(5)	117.4(5)	117.1(4)
C(8) – N(2) – C(11)	108.8(4)	108.8(4)	108.8(4)	109.0(4)	109.0(4)
C(16) – N(3) – C(19)	109.1(4)	108.6(4)	108.7(4)	108.6(4)	108.5(4)
C(3) – C(7) – C(9)	111.6(4)	110.8(4)	110.8(4)	111.3(4)	111.1(4)
C(3) – C(7) – C(17)	112.5(4)	112.9(4)	112.8(4)	112.7(4)	113.2(4)
C(9) – C(7) – C(17)	114.2(3)	114.6(4)	114.6(4)	114.4(4)	114.3(4)

Table S9 Hydrogen bond lengths (Å) and angles (°) of **O(1)−H···N(1)** for the same single crystal of **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

Irradiation time	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
As-prepared	1.71(6)	2.704(6)	168(4)
25 min	1.93(5)	2.712(6)	160(6)
40 min	1.90(5)	2.706(6)	167(5)
80 min	1.90(5)	2.701(6)	165(5)
2 weeks	1.92(5)	2.708(6)	162(5)

Table S10 Hydrogen bond lengths (Å) and angles (°) of **N(2)−H···O(1)** for the same single crystal of **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

Irradiation time	**d(H···A)**/Å	**d(D···A)**/Å	**<(DHA)**/°
As-prepared	2.195(5)	3.013(5)	158.7(5)
25 min	2.189(6)	3.007(5)	158.7(5)
40 min	2.184(6)	3.003(5)	159.0(5)
80 min	2.186(6)	3.006(5)	159.3(5)
2 weeks	2.180(6)	3.002(5)	159.7(5)

Table S11 Hydrogen bond lengths (Å) and angles (°) of **N(3)−H···O(1)** for the same single crystal of **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

Irradiation time	**d(H···A)**/Å	**d(D···A)**/Å	**<(DHA)**/°
As-prepared	2.301(5)	2.990(5)	137.1(4)
25 min	2.301(6)	2.985(6)	136.7(5)
40 min	2.300(6)	2.987(6)	137.0(4)
80 min	2.296(6)	2.981(6)	136.7(5)
2 weeks	2.291(6)	2.981(6)	137.2(4)

Table S12 CH···cg distances of π-interactions (Å) for the same single crystal of **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

PMDI·MeOH/ PMDI·MeOH´					
π-interaction	**As-prepared**	**25 min**	**40 min**	**80 min**	**2 weeks**
C(4) − H···cg(5)	2.634(5)	2.636(5)	2.628(5)	2.622(5)	2.619(5)
C(5) − H···cg(1)	2.983(6)	2.985(6)	2.986(6)	2.978(6)	2.975(6)
C(6) − H···cg(4)	2.988(6)	2.971(7)	2.975(6)	2.976(7)	2.964(6)
C(8) − H···cg(2)	2.855(5)	2.851(5)	2.850(5)	2.844(5)	2.849(5)
C(12) − H ···cg(4)	3.698(5)	3.680(5)	3.688(5)	3.668(5)	3.675(5)
cg(4)···cg(4)	3.921(3)	3.917(4)	3.920(4)	3.916(4)	3.924(3)

Table S13 Selected distances and dihedral angles (°) at S_0 and S_1 optimized geometries computed at B3LYP/6-311G(d) and TD-B3LYP/6-311G(d) levels.

Molecule	S_0 state					
	Distance (Å)			Dihedral angle (°)		
	N(2)···O(1)	**N(3)···O(1)**	**O(1)···N(1)**	**N(2)H···O(1)**	**N(3)H···O(1)**	**O(1)H···N(1)**
PMDI:MeOH-a	2.902	-	-	172.0	-	-
PMDI:MeOH-b	-	2.902	-	-	170.5	-
PMDI:MeOH-c	-	-	2.862	-	-	157.9
PMDI:2MeOH-ab	2.907	2.903	-	171.0	169.1	-
PMDI:2MeOH-ac	2.898	-	2.860	170.2	-	158.9
PMDI:2MeOH-bc	-	2.891	2.862	-	166.2	158.6
PMDI:3MeOH	2.904	2.896	2.859	170.3	165.8	159.8
	S_1 state					
	Distance (Å)			Dihedral angle (°)		
	N(2)···O(1)	**N(3)···O(1)**	**O(1)···N(1)**	**N(2)H···O(1)**	**N(3)H···O(1)**	**O(1)H···N(1)**
PMDI:MeOH-a	2.828	-	-	175.6	-	-
PMDI:MeOH-b	-	2.805	-	-	170.1	-
PMDI:MeOH-c	-	-	2.718	-	-	161.3
PMDI:2MeOH-ab	2.889	2.811	-	155.0	171.1	-
PMDI:2MeOH-ac	2.825	-	2.713	176.6	-	162.1
PMDI:2MeOH-bc	-	2.716	2.653	-	145.5	162.2
PMDI:3MeOH	2.859	2.773	2.665	173.1	141.5	162.7

Table S14 Theoretical absorption data for S_0 state, oscillator strength (f), and molecular orbitals (MOs) contribution calculated by TD-B3LYP/6-311G(d) level.

Molecule	λ_{abs} (nm)	f	MOs contribution	Character
PMDI	260	0.062	H-1→L+3 (72%)	^{1}LLCT
	368	0.004	H→L (97%)	^{1}LLCT
PMDI·MeOH-a	266	0.063	H-1→L+1 (55%)	π-π* IL
	301	0.011	H→L (96%)	^{1}LLCT
PMDI·MeOH-b	268	0.058	H→L+3 (82%)	π-π* IL
	310	0.004	H→L (98%)	^{1}LLCT
PMDI·MeOH-c	261	0.063	H-1→L+2 (81%)	π-π* IL
	319	0.004	H→L (99%)	^{1}LLCT
PMDI·2MeOH-ab	266	0.064	H-1→L+2 (76%)	π-π* IL
	311	0.003	H→L (98%)	^{1}LLCT
PMDI·2MeOH-ac	264	0.050	H-1→L+2 (88%)	π-π* IL
	324	0.007	H→L (94%)	^{1}LLCT
PMDI·2MeOH-bc	262	0.063	H-1→L+2 (81%)	π-π* IL
	339	0.007	H→L (99%)	^{1}LLCT
PMDI·3MeOH	265	0.064	H-1→L+2 (87%)	π-π* IL
	339	0.005	H→L (99%)	^{1}LLCT

Table S15 Theoretical absorption data for S_1 state, oscillator strength (f), and molecular orbitals (MOs) contribution calculated by TD-B3LYP/6-311G(d) level.

Molecule	λ_{emiss} (nm)	f	MOs contribution	Character
PMDI	282	0.065	H→L+2 (64%)	π-π* IL
	368	0.002	H→L (100%)	^{1}LLCT
PMDI·MeOH-a	301	0.056	H→L+3 (90%)	π-π* IL
	413	0.012	H→L (100%)	^{1}LLCT
PMDI·MeOH-b	286	0.083	H→L+3 (86%)	π-π* IL
	388	0.002	H→L (100%)	^{1}LLCT
PMDI·MeOH-c	263	0.037	H-1→L+1 (59%)	π-π* IL
	447	0.005	H→L (100%)	^{1}LLCT
PMDI·2MeOH-ab	287	0.079	H→L+3 (90%)	π-π* IL
	397	0.001	H→L (100%)	^{1}LLCT
PMDI·2MeOH-ac	302	0.062	H→L+3 (93%)	π-π* IL
	474	0.004	H→L (100%)	^{1}LLCT
PMDI·2MeOH-bc	294	0.053	H→L+3 (92%)	π-π* IL
	515	0.003	H→L (100%)	^{1}LLCT
PMDI·3MeOH	303	0.035	H→L+3 (78%)	π-π* IL
	553	0.008	H→L (100%)	^{1}LLCT

Table S16 HOMO and LUMO energy levels (eV) at S_0 and S_1 optimized geometries calculated by TD-B3LYP/6-311G(d) level.

Molecule	S_0 state			S_1 state		
	HOMO	**LUMO**	**E_g**	**HOMO**	**LUMO**	**E_g**
PMDI	-5.55	-0.74	4.82	-5.21	-1.21	4.00
PMDI·MeOH-a	-5.32	-0.60	4.72	-4.69	-1.08	3.62
PMDI·MeOH-b	-5.20	-0.59	4.61	-4.85	-1.03	3.82
PMDI·MeOH-c	-5.59	-1.09	4.50	-5.04	-1.65	3.39
PMDI·2MeOH-ab	-5.06	-0.45	4.61	-4.75	-1.00	3.75
PMDI·2MeOH-ac	-5.39	-0.96	4.43	-4.77	-1.54	3.23
PMDI·2MeOH-bc	-5.24	-0.96	4.28	-4.86	-1.82	3.03
PMDI·3MeOH	-5.11	-0.83	4.27	-4.56	-1.71	2.86

Figures S1-S19

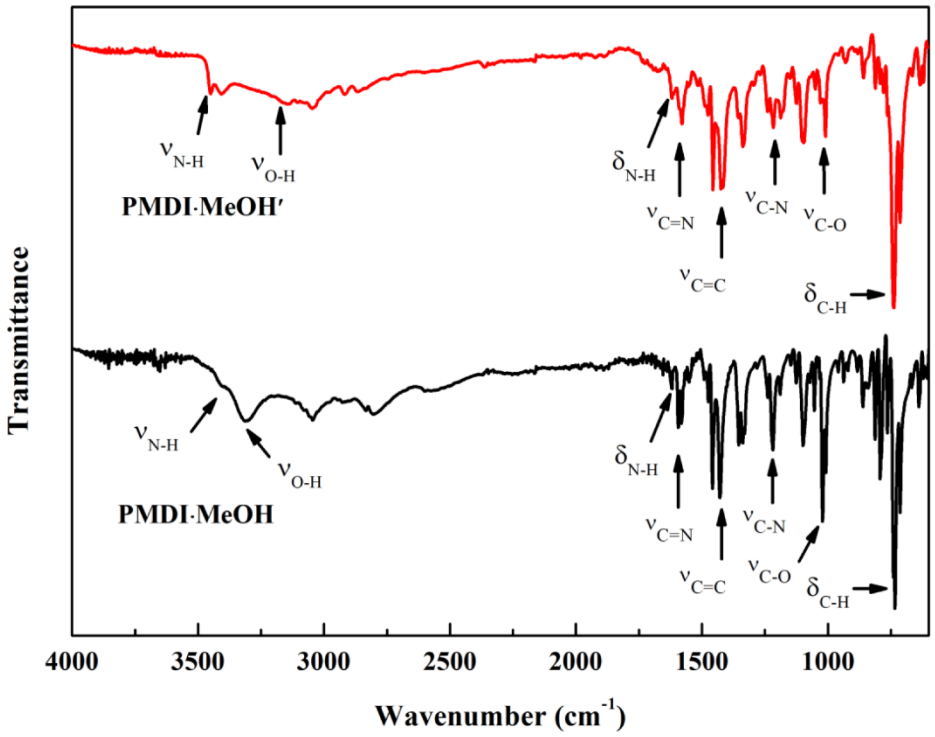

Figure S1 The comparison of FTIR spectra of **PMDI·MeOH** and **PMDI·MeOH´.**

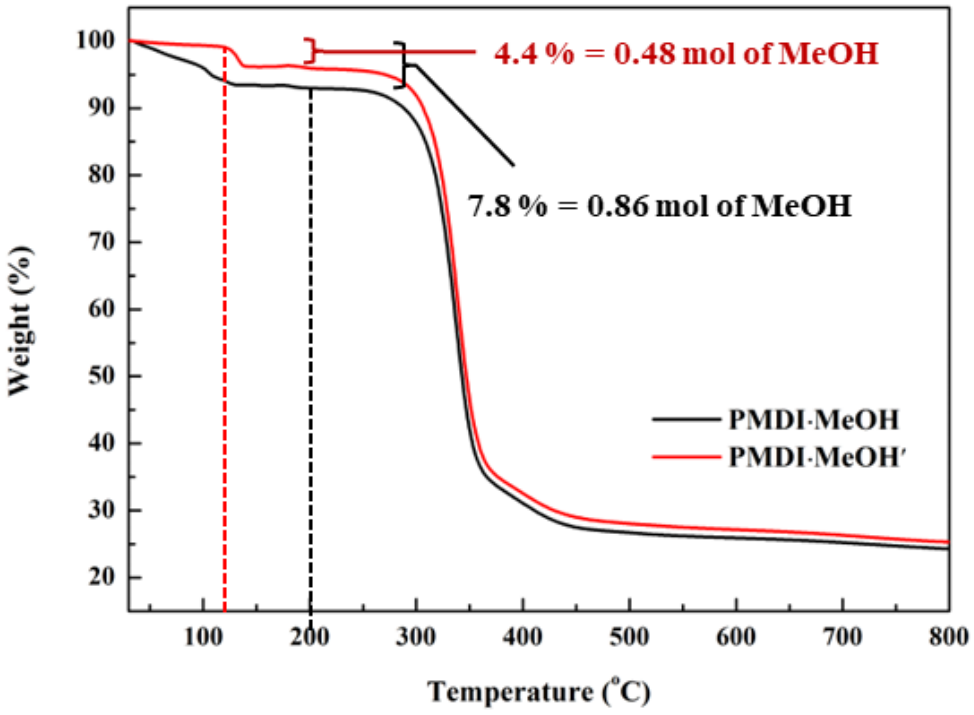

Figure S2 The comparison of thermograms of **PMDI·MeOH** and **PMDI·MeOH´.**

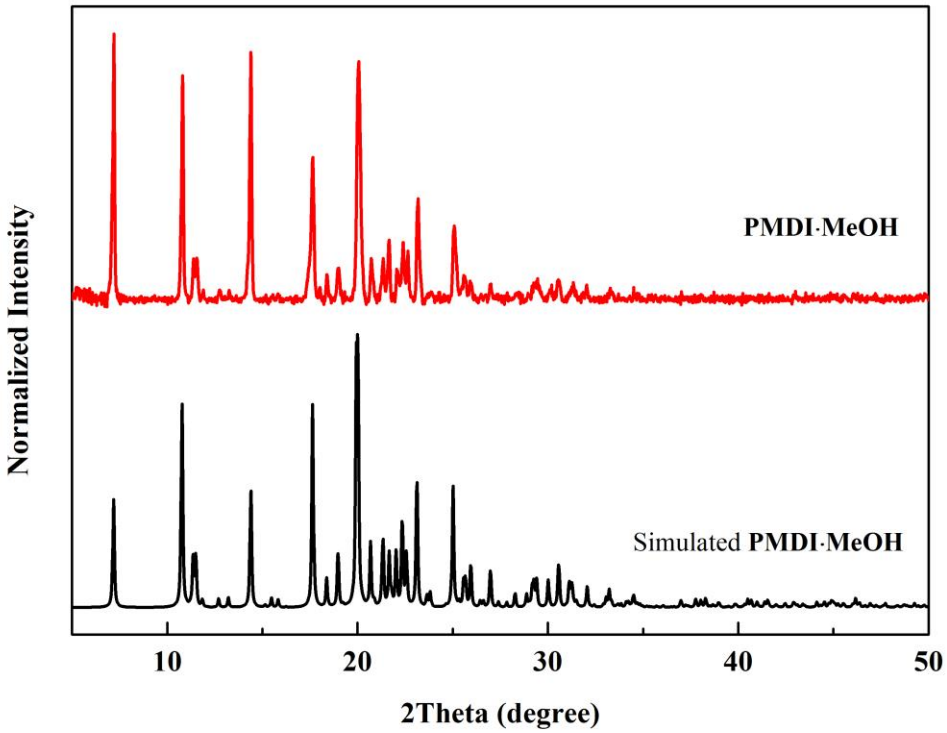

Figure S3 The PXRD pattern of **PMDI·MeOH**.

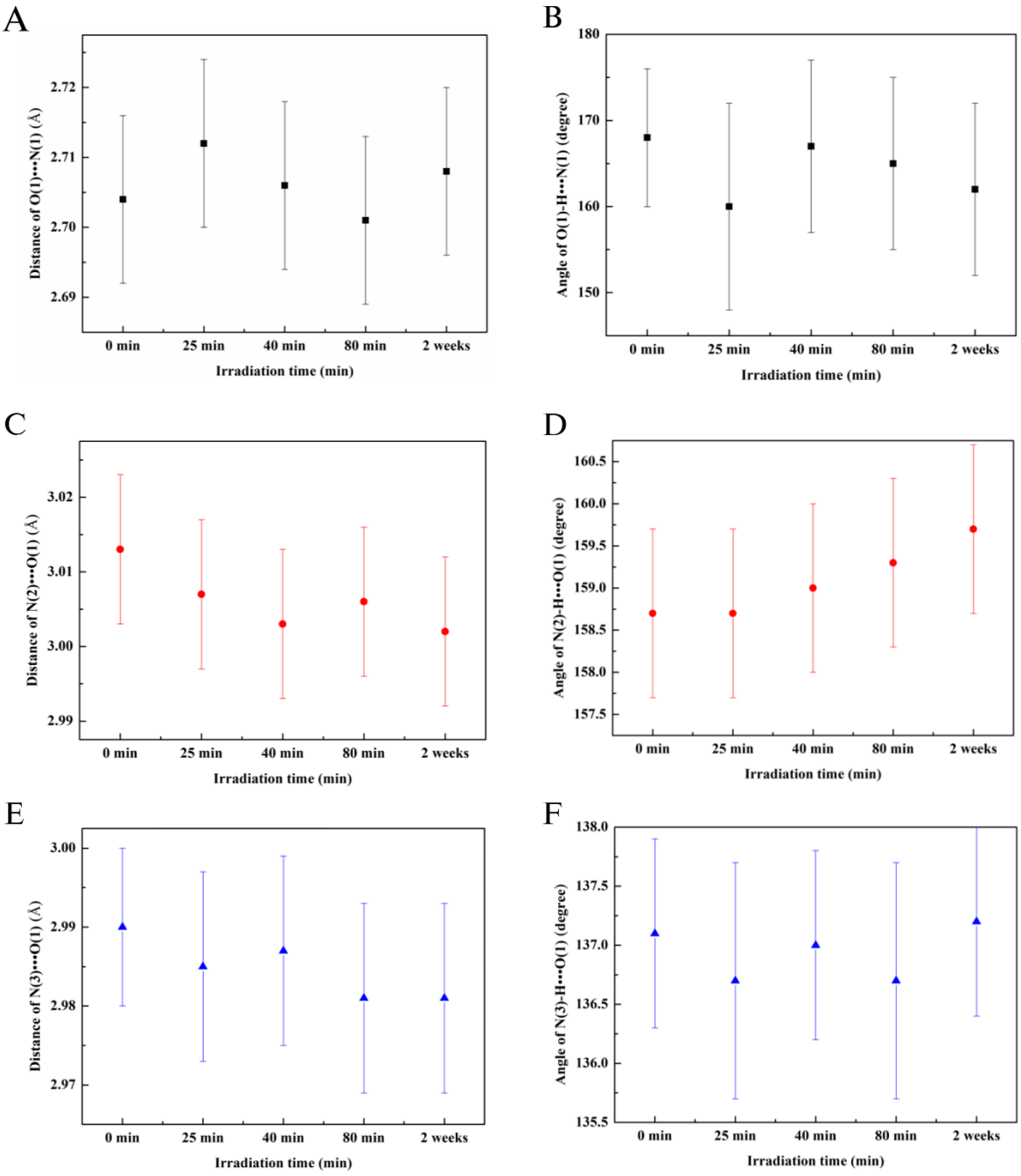

Figure S4 The variations of hydrogen bonds for **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

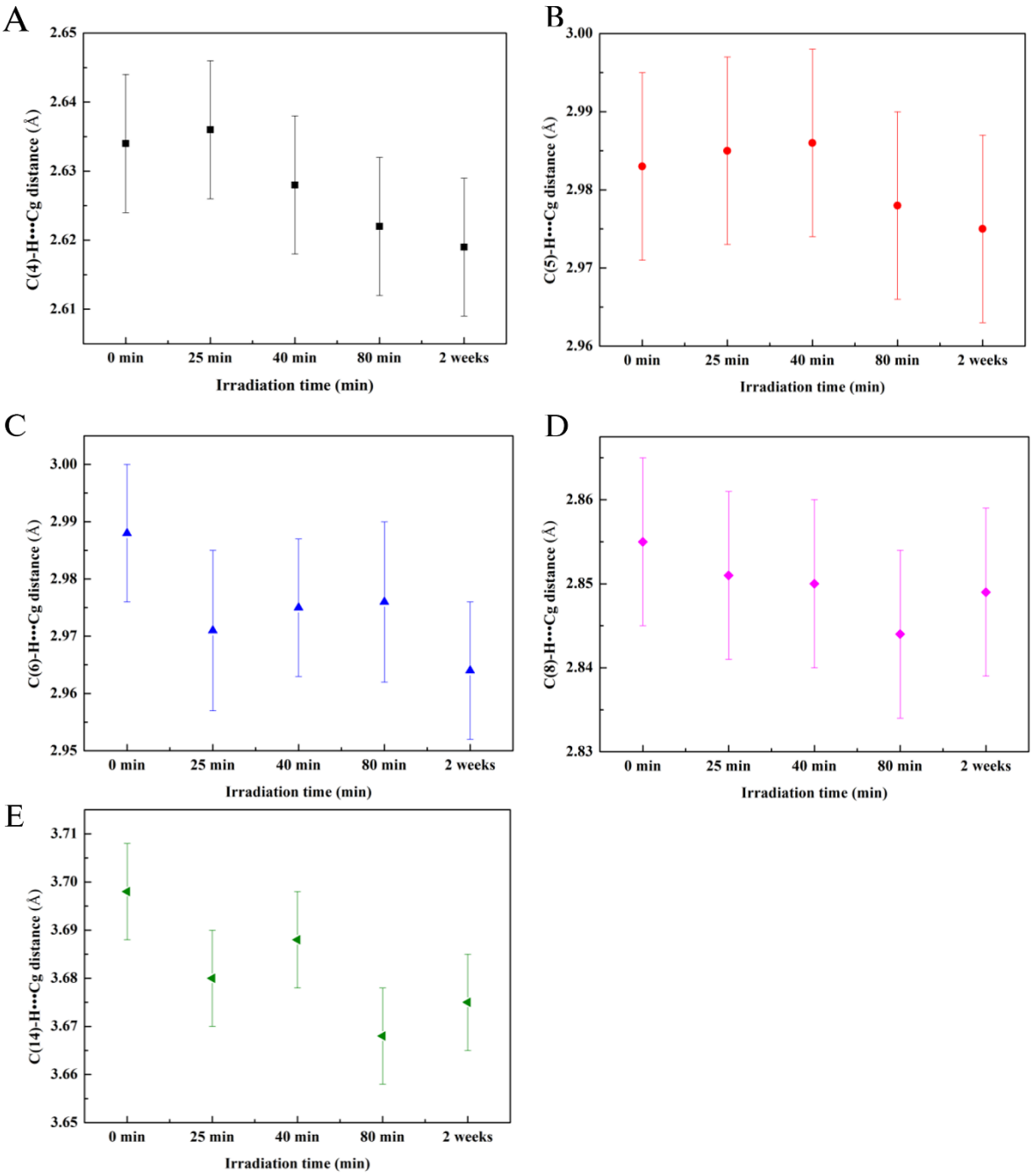

Figure S5 The variations of CH-π interactions for **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

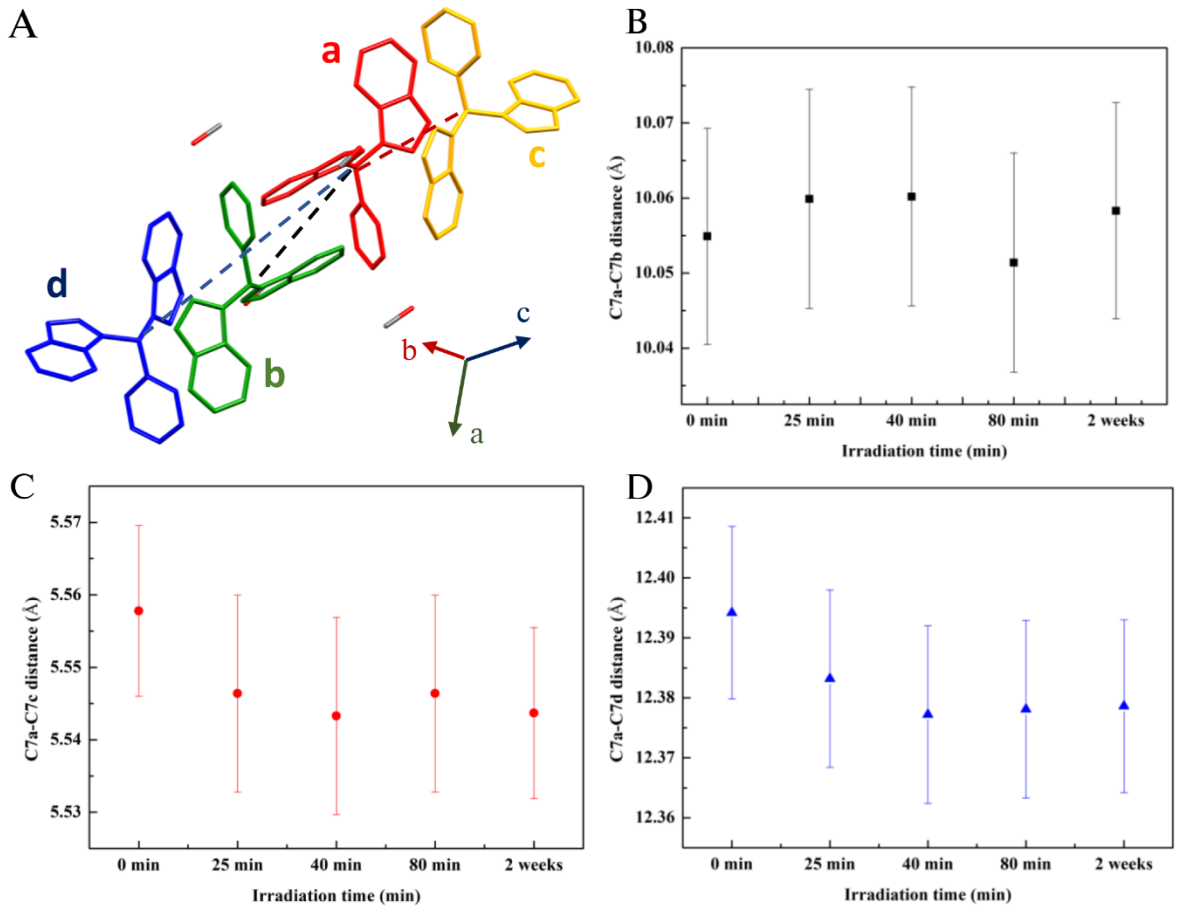

Figure S6 The shortened distances between three adjacent PMDI molecules measured between C(7) atoms of **PMDI** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

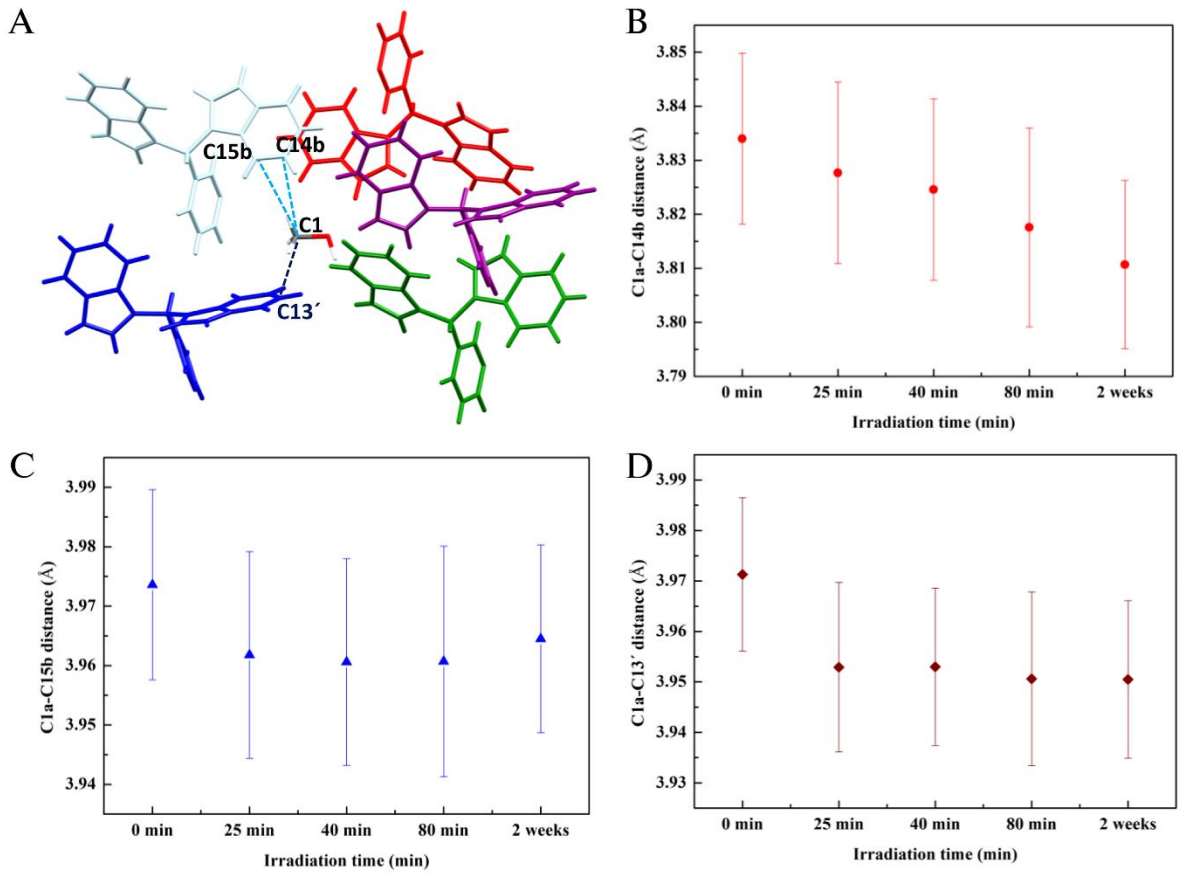

Figure S7 The variations of short contacts around C(1) atom of methanol in **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

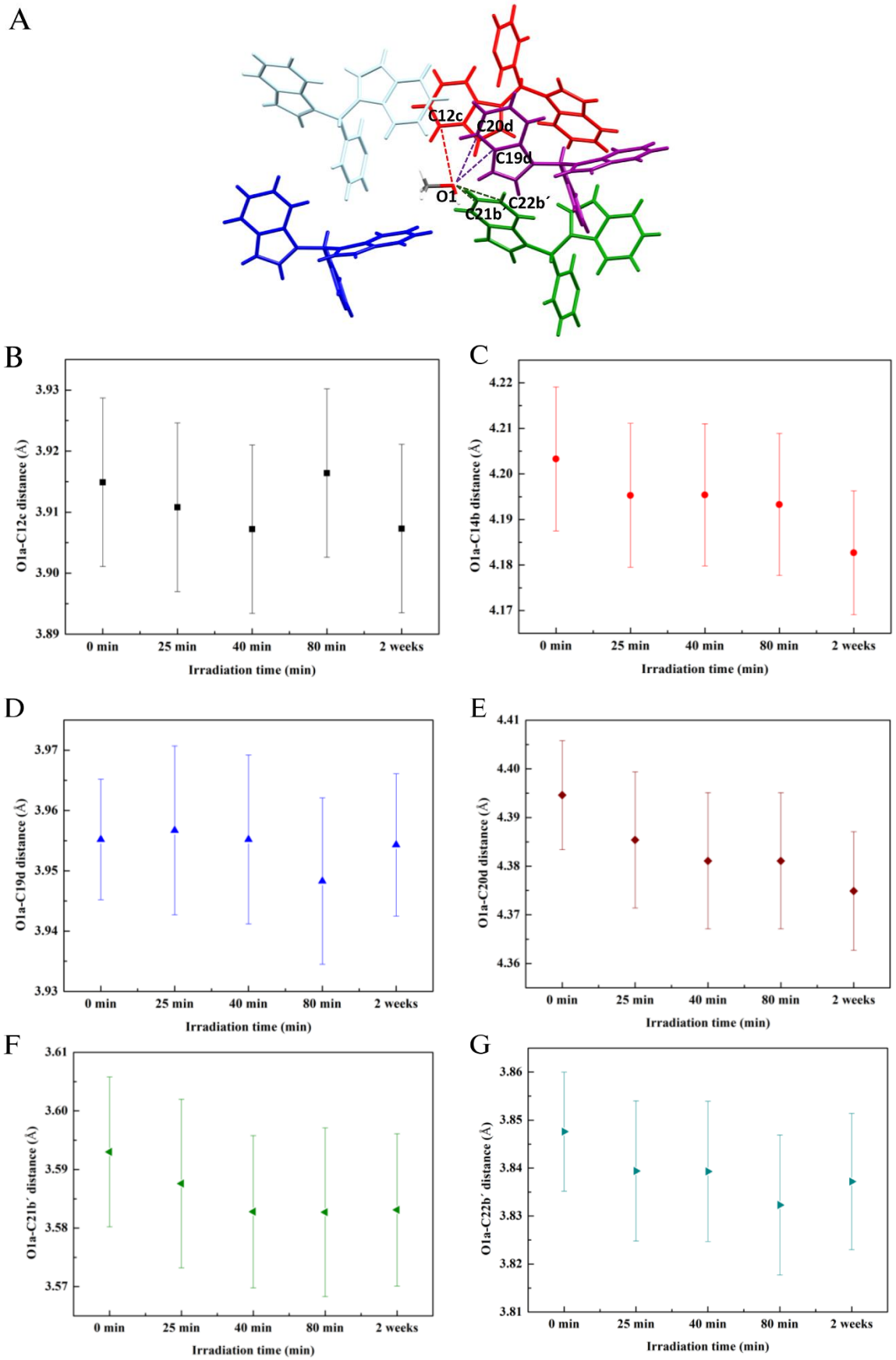

Figure S8 The variations of short contacts around O(1) atom of methanol in **PMDI·MeOH** at various irradiation times and irradiated **PMDI·MeOH** that was left under ambient light for 2 weeks.

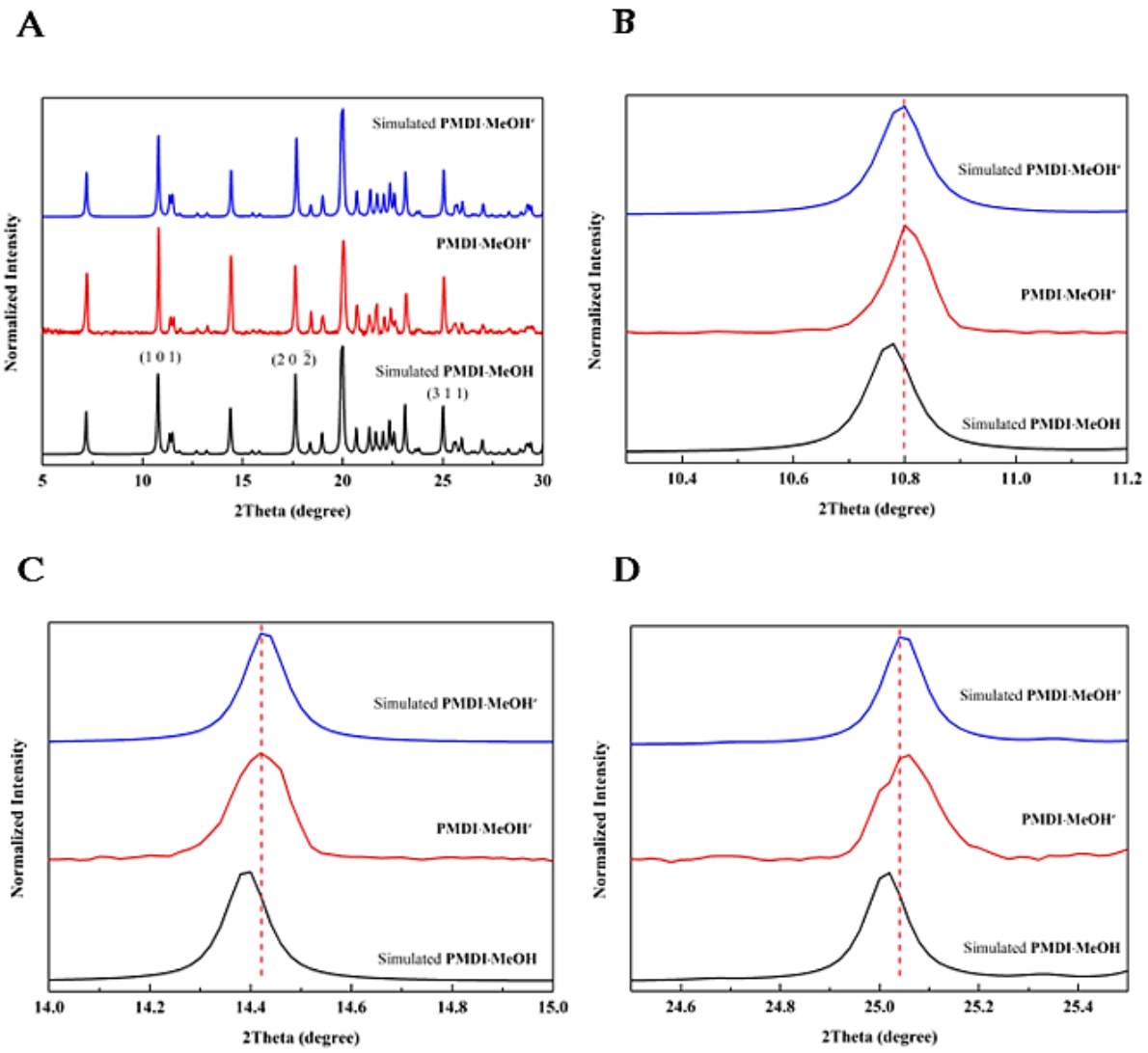

Figure S9 (A) The PXRD patterns of **PMDI·MeOH´** and close-up diffraction peaks of (B) (101), (C) (20-2), and (D) (311) .

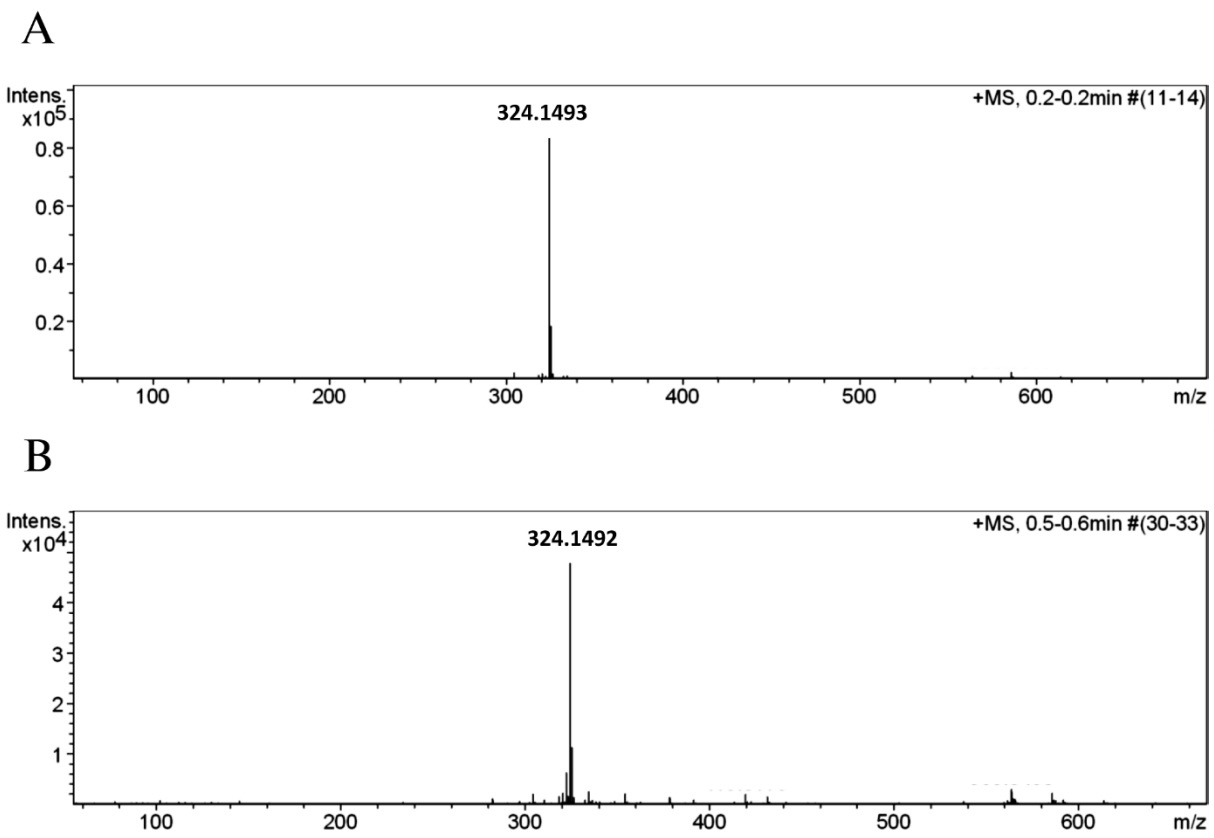

Figure S10 The ESI-MS spectra of (A) **PMDI·MeOH** and (B) **PMDI·MeOH´**.

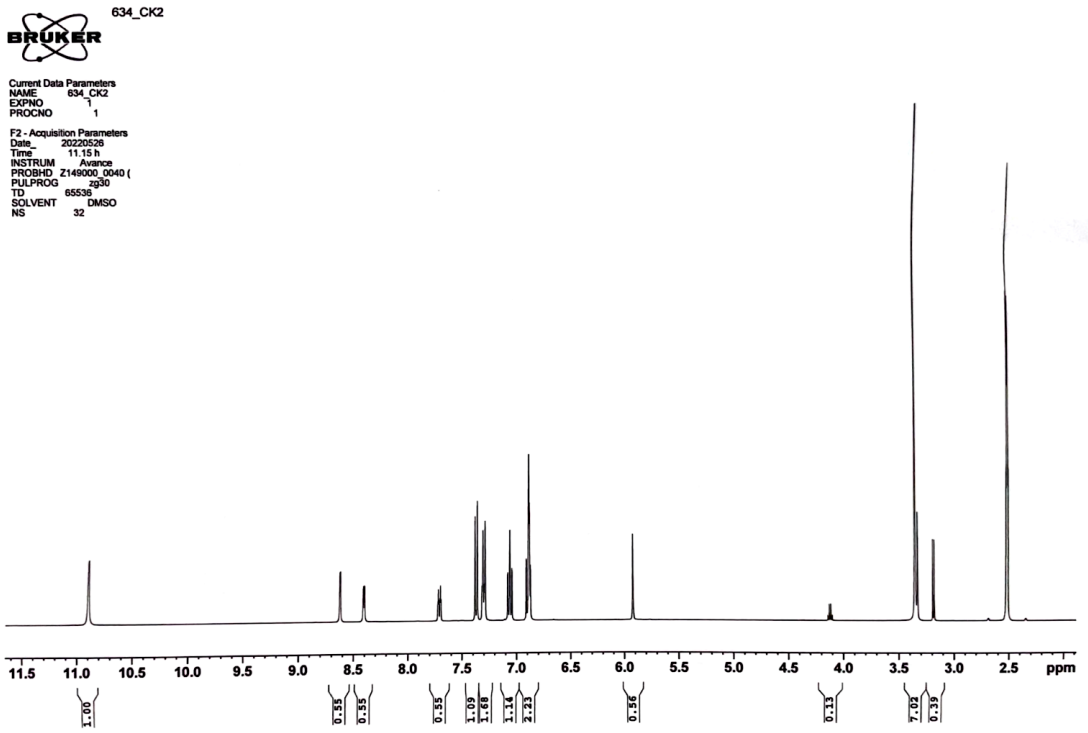

Figure S11 ^{1}H-NMR spectrum of synthesized **PMDI**.

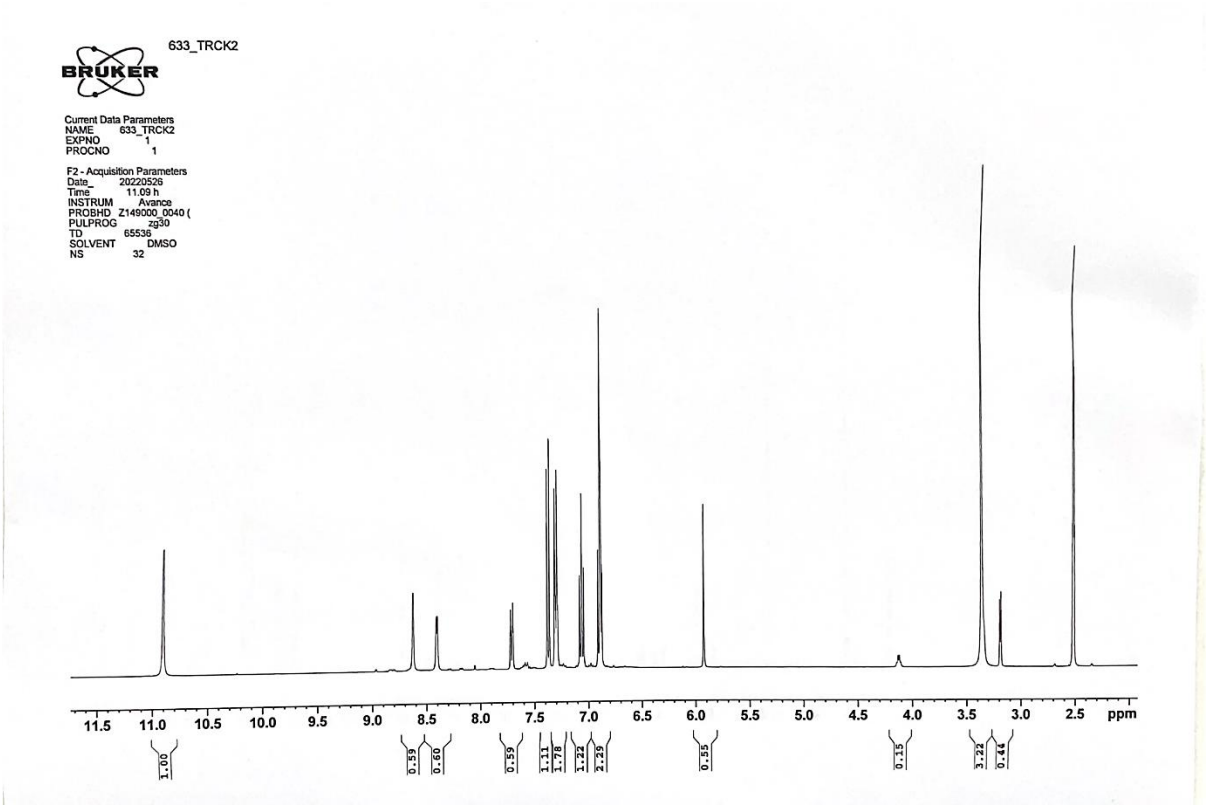

Figure S12 ^{1}H-NMR spectrum of synthesized **PMDI´**.

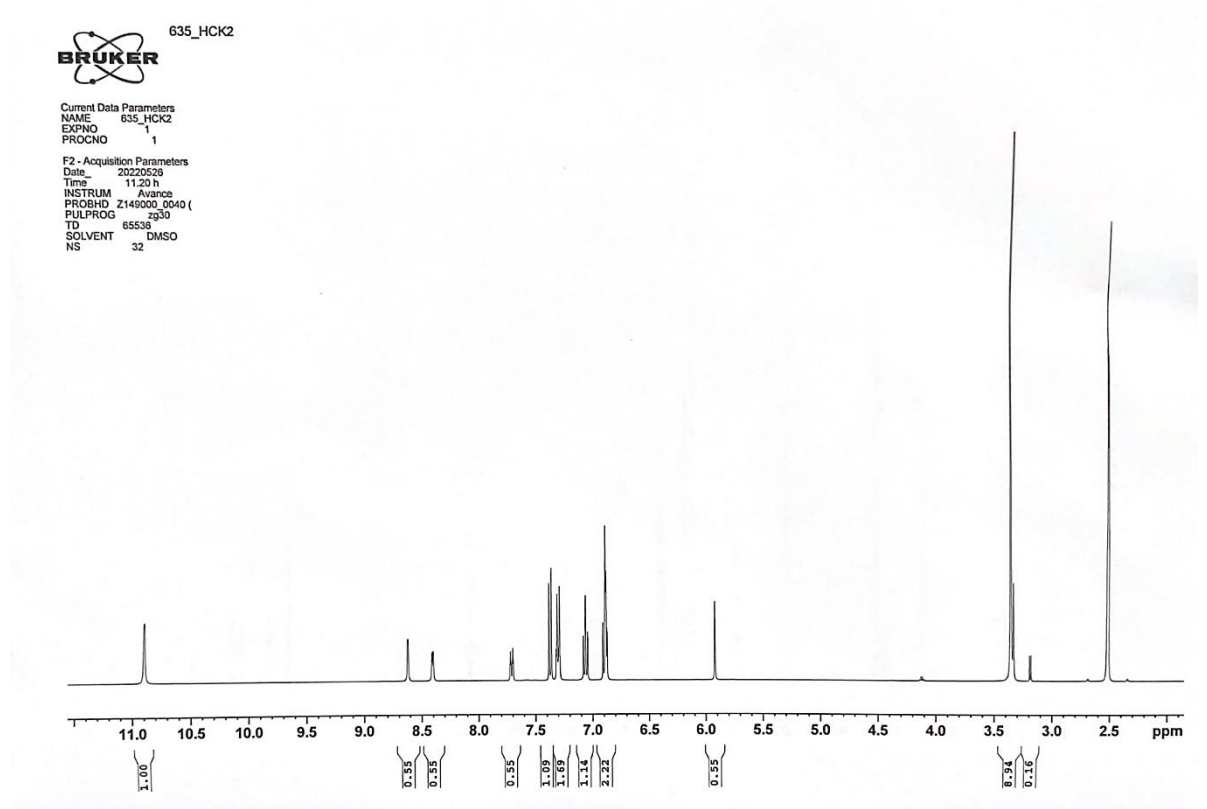

Figure S13 ^{1}H-NMR spectrum of synthesized **PMDI˝**.

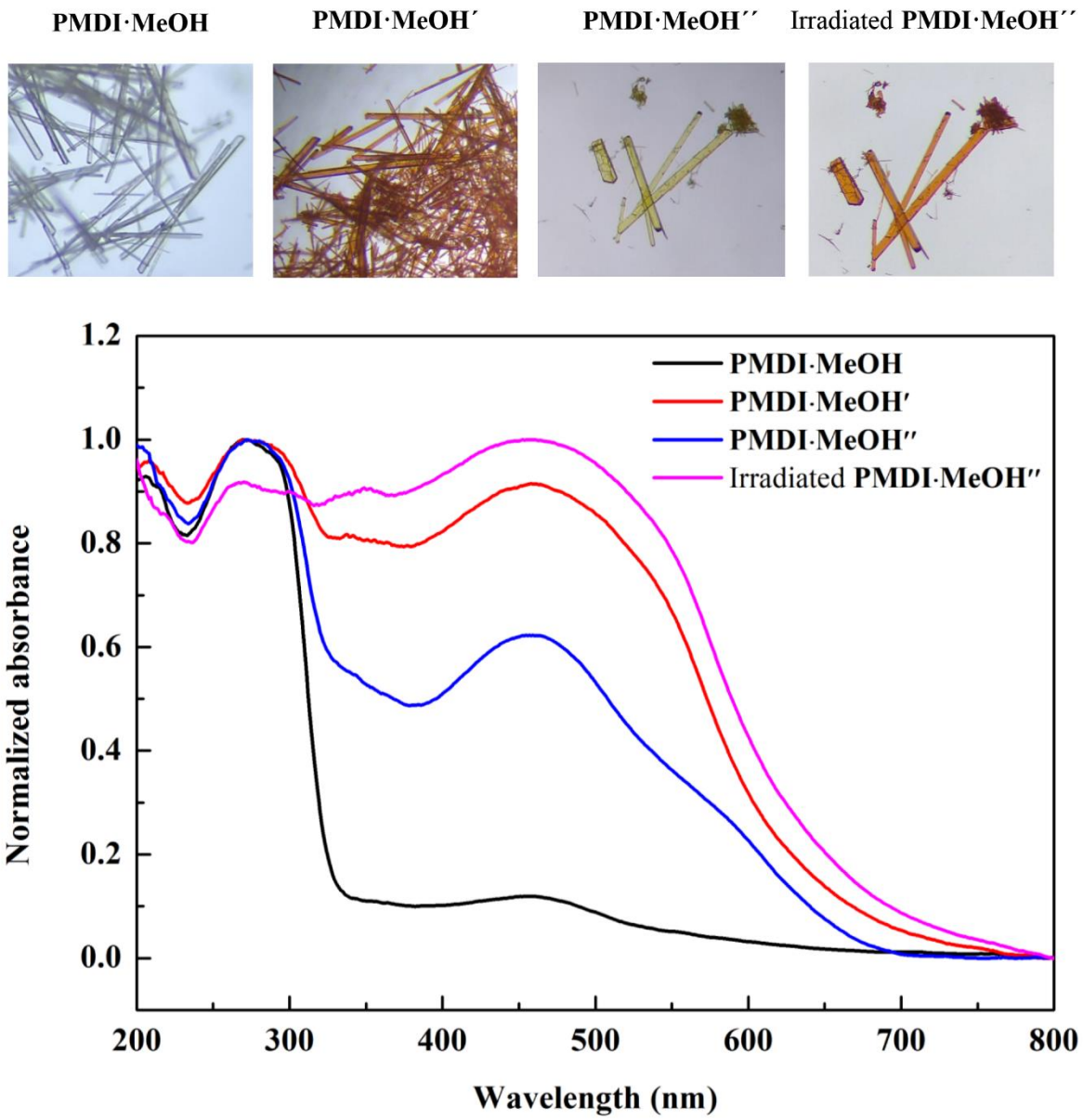

Figure S14 The color change of **PMDI·MeOH** upon UV irradiation and heating and the diffuse reflectance spectra of as-prepared, irradiated, heated **PMDI·MeOH** and irradiation treatment after heating of **PMDI·MeOH**.

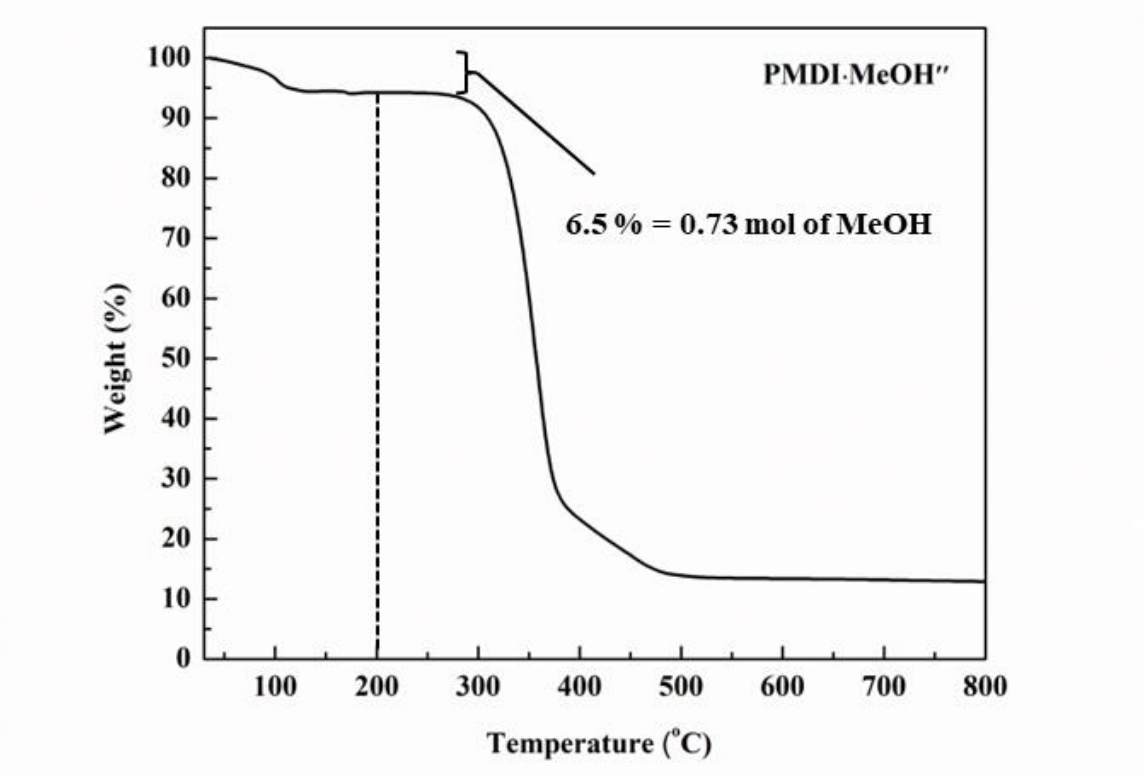

Figure S15 The thermogram of **PMDI·MeOH´´.**

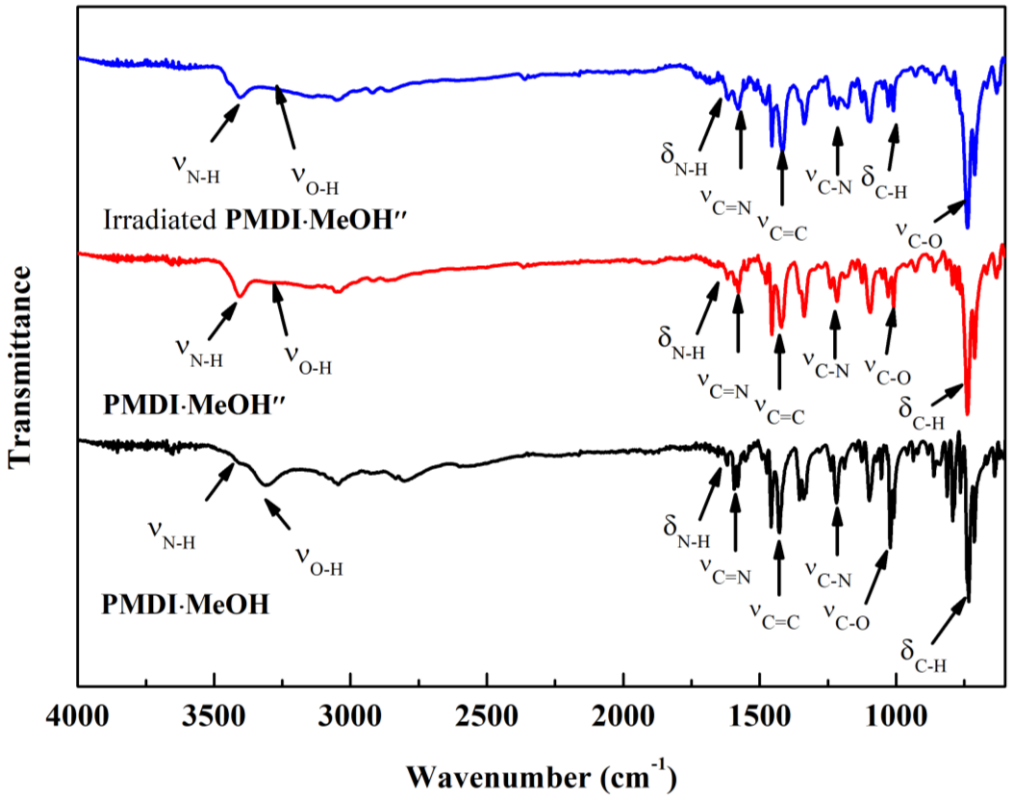

Figure S16 The comparison of FTIR spectra of **PMDI·MeOH**, **PMDI·MeOH´´** and irradiated **PMDI·MeOH´´**.

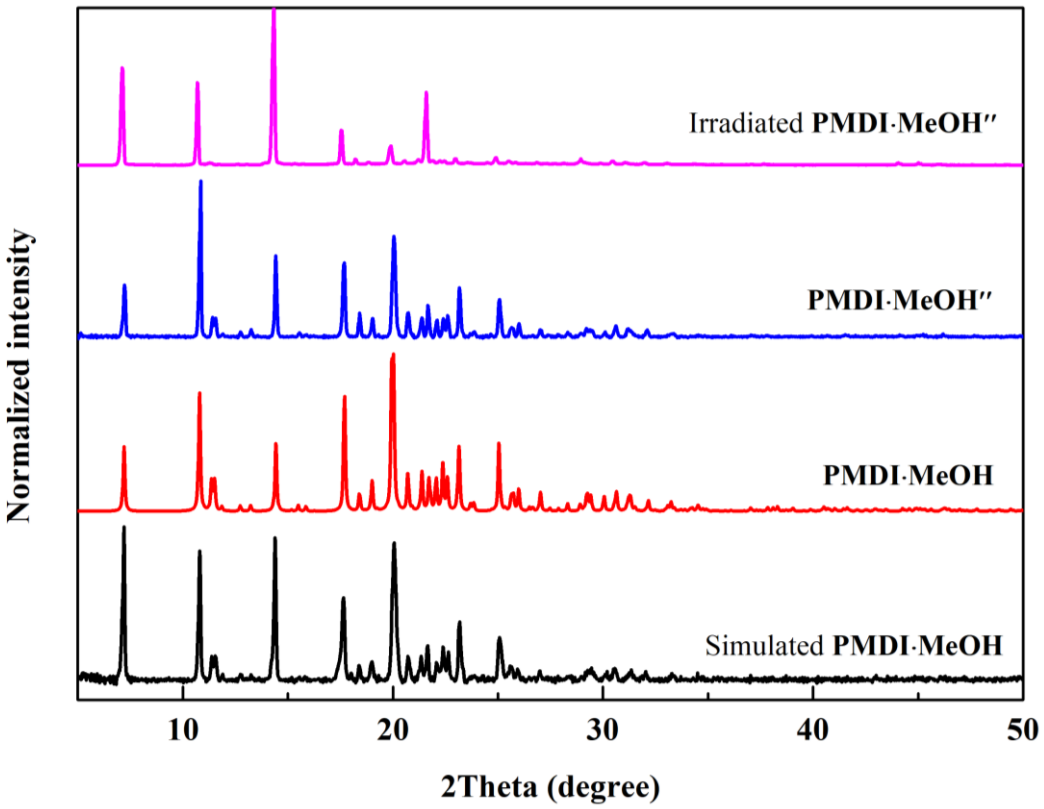

Figure S17 The comparison of PXRD patterns of **PMDI·MeOH**, **PMDI·MeOH**′′ and irradiated **PMDI·MeOH**′′.

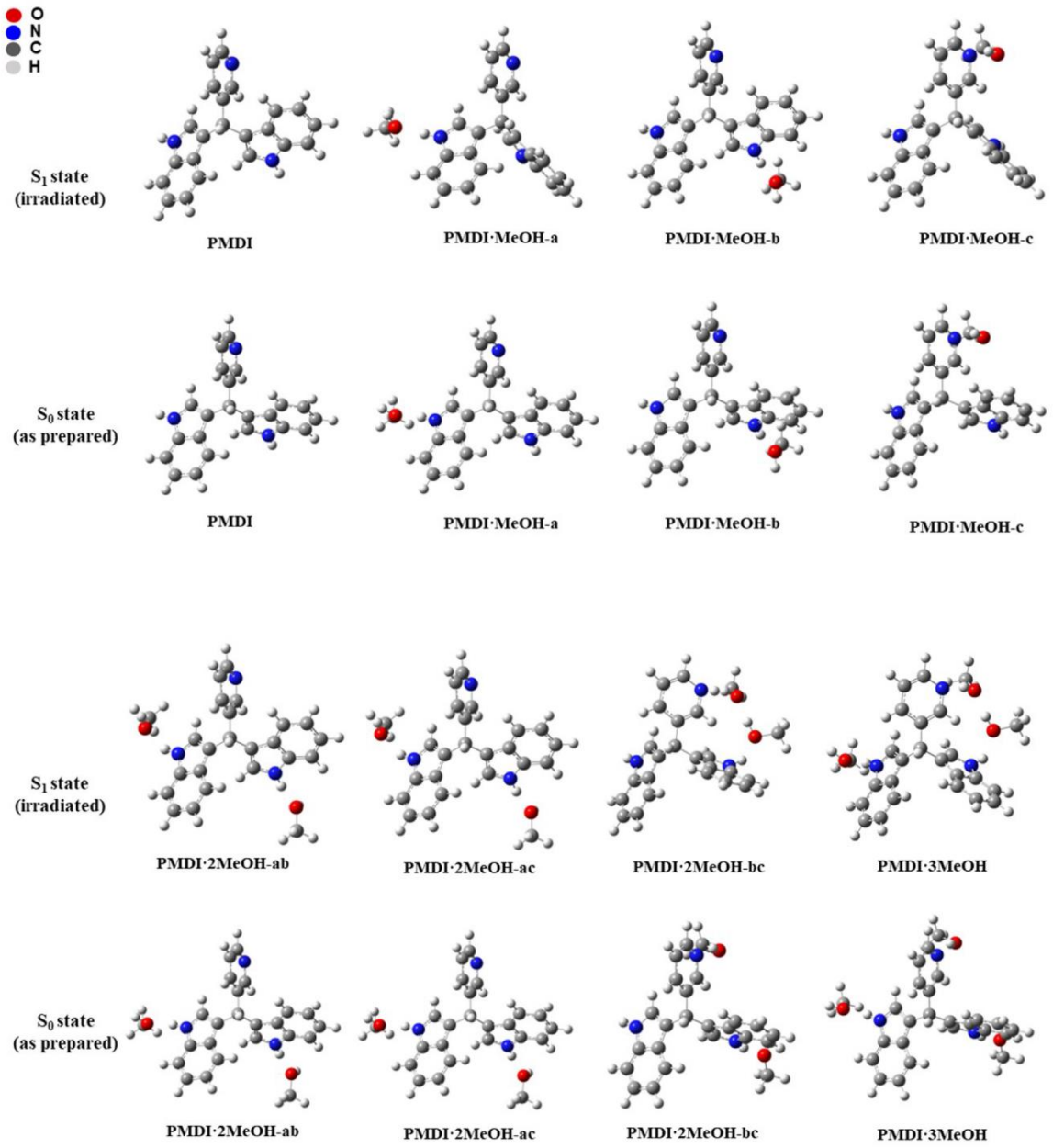

Figure S18 S_0 and S_1 optimized geometries computed at B3LYP/6-311G(d) level.

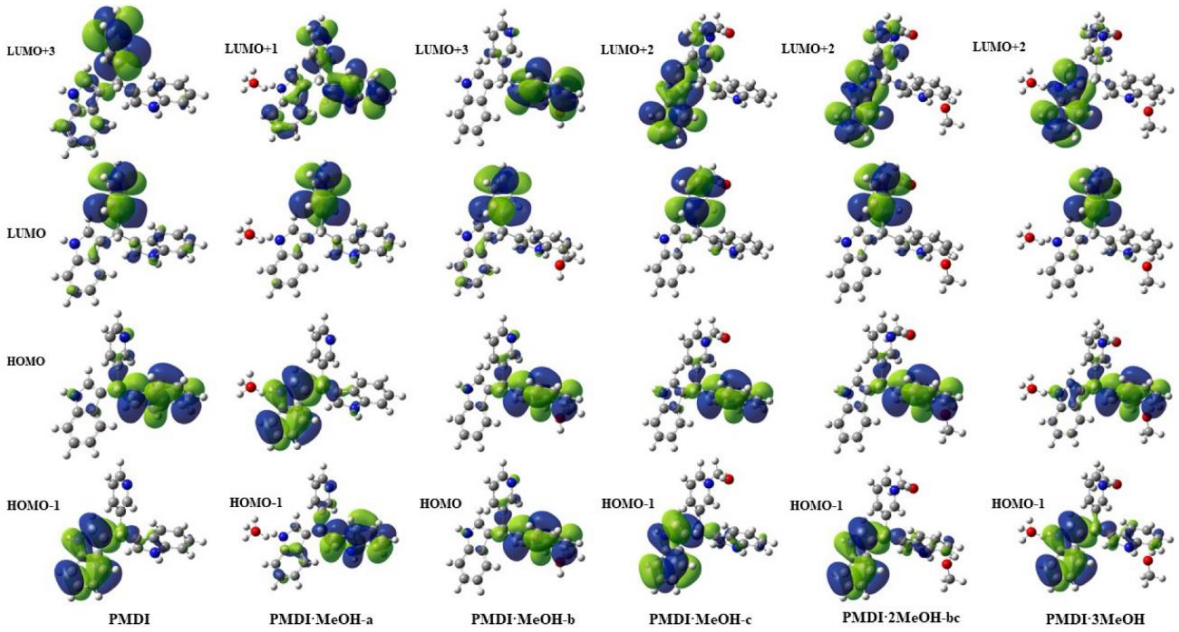

Figure S19 HOMO and LUMO orbitals and frontier MOs corresponding to the main transition of absorption spectra at S_0 optimized geometries computed at TD-B3LYP/6-311G(d) level.

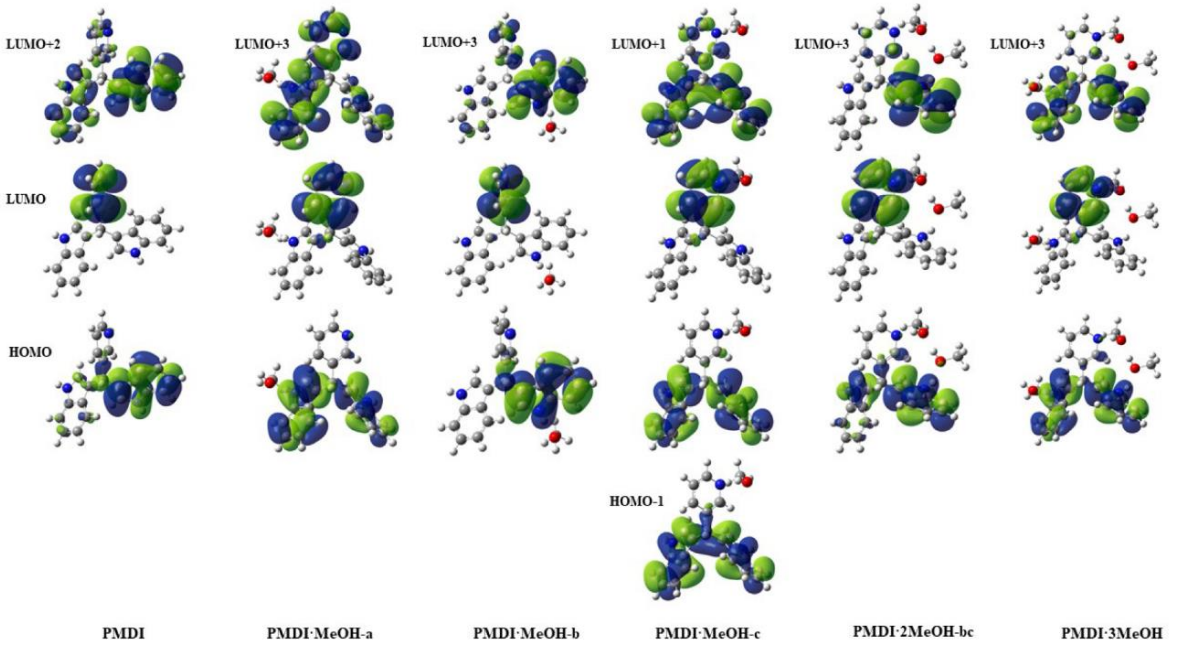

Figure S20 HOMO and LUMO orbitals and frontier MOs corresponding to the main transition of absorption spectra at S_1 optimized geometries computed at TD-B3LYP/6-311G(d) level.