Supporting Information

Unexpected Molecular Flip in Solid-State Photodimerization

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Table S1. The crystal data of 1,1,6,6-Tetraphenyl-2,4-hexadiyne-1,6-diol:6-Methyl-2(1H)-Pyridinone (**I-a**).

$C_{30}H_{22}O_2 \cdot 2(C_7H_9NO)$					
Temperature (K)	100	293	293	293	100
Formula weight	660.78	660.78	660.78	660.78	660.78
Crystal colour	colourless	colourless	colourless	colourless	colourless
Crystal size (mm)	0.32x0.26x0.14	0.32x0.26x0.14	0.32x0.26x0.14	0.32x0.26x0.14	0.32x0.26x0.14
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å), (°)					
a =	10.3620 (7)	10.357 (2)	10.330 (1)	10.299 (14)	10.238 (8)
b =	8.4440 (3)	8.934 (2)	9.063 (2)	9.106 (6)	9.059 (6)
c =	22.2770 (14)	20.857 (4)	20.302 (2)	20.111 (17)	19.82 (2)
β =	117.355 (2)	114.571 (4)	113.699 (3)	113.26 (4)	112.86 (4)
Volume (Å^3)	1731.20 (17)	1755.1 (6)	1740.4 (3)	1733 (3)	1694 (3)
Z	2	2	2	2	2
Diffractometer	APEX DUO	APEX DUO	APEX DUO	Nonius KappaCCD	Nonius KappaCCD
Wavelength MoKα, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.08	0.08	0.08	0.08	0.08
2θ max (°)	50.6	54.8	59.8	49.4	49.6
Min./Max. indices h,k,l	-12/12,-9/10,-26/26	-12/13,-11/11,-18/26	-13/14,-12/12,-28/25	0/12,-10/0,-23/20	0/12,-10/0,-23/20
Reflections collected/unique	6022 / 3151	7043 / 4004	11345 / 5018	12299 / 2933	11919 / 2881
R_{int}	0.026	0.032	0.026	0.044	0.065
Observed reflections (I>2σ(I))	2105	2276	3160	2065	1934
Data/parameters/restrains	3151 / 307 / 0	3926 / 263 / 0	5018 / 263 / 0	2933 / 228 / 0	2881 / 226 / 0
Goodness of fit on F^2	1.11	0.99	1.07	0.99	0.94
Final R_1 indices (I>2σ(I))	0.070	0.076	0.064	0.041	0.046
wR_2 indices	0.228	0.251	0.216	0.124	0.134
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0. 31, -0.27	0. 35, -0.30	0. 38, -0.26	0. 15, -0.15	0. 15, -0.20
Weighting scheme: x; y[a]	0.1382 / 0.0886	0.1625 / 0.0	0.1328 / 0.0	0.0775 / 0.0741	0.0838 / 0.0
Extinction coefficient	-	-	-	-	-

[a] $w = 1/[(\sigma^2(Fo^2)+(xP)^2 + yP]$, where $P=(Fo^2+2Fc^2)/3$.

Table S2. The crystal data of 1,1,6,6-Tetraphenyl-2,4-hexadiyne-1,6-diol : 2(1,6-dimethyl-2(1H)-pyridone) (**I-b**) at different temperatures.

$C_{30}H_{22}O_2 \cdot 2(C_6H_7NO)$				
Temperature (K)	290	313	353	393
Formula weight	632.73	632.73	632.73	632.73
Crystal colour	colourless	colourless	colourless	colourless
Crystal size (mm)	0.46x0.28x0.16	0.46x0.28x0.16	0.46x0.28x0.16	0.46x0.28x0.16
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	*P-1*	*P-1*	*P-1*	*P-1*
Unit cell dimensions (Å), (°)				
a =	8.454 (10)	8.46 (2)	8.47 (2)	8.4750 (5)
b =	10.833 (12)	10.84 (3)	10.85 (3)	10.8530 (6)
c =	11.37 (2)	11.35 (3)	11.36 (2)	11.360 (1)
α =	63.86 (4)	64.31 (11)	64.56 (10)	64.798 (3)
β =	79.73 (5)	80.49 (8)	80.82 (7)	81.182 (2)
γ =	68.44 (3)	68.68 (6)	68.92 (6)	69.185 (7)
Volume (Å^3)	869 (2)	874 (4)	879 (3)	883.72 (11)
Z	1	1	1	1
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Wavelength MoKα, λ (Å)	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.08	0.08	0.08	0.08
2θ max (°)	50.0	49.4	49.4	50.4
Min./Max. indices h,k,l	0/10,-11/12,-12/13	0/9,-11/12,-12/13	0/9,-11/12,-12/13	0/9,-11/12,-12/13
Reflections collected/unique	7693 / 3042	10382 / 2930	10498 / 2974	9264 / 2986
R_{int}	0.036	0.049	0.051	0.055
Observed reflections (I>2σ(I))	1872	1572	1569	1327
Data/parameters/restrains	3042 / 235 / 8	2930 / 234 / 8	2974 / 235 / 8	2986 / 235 / 8
Goodness of fit on F^2	0.99	0.81	0.89	0.91
Final R_1 indices (I>2σ(I))	0.046	0.051	0.0.050	0.055
wR_2 indices	0.139	0.182	0.172	0.183
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0. 13, -0.16	0.16, -0.21	0.14,-0.17	0.13, -0.13
Weighting scheme: x; y[a]	0.0796	0.129	0.1094	0.0996
Extinction coefficient	0.047 (10)	–	0.074 (15)	0.031 (7)

[a] $w = 1/(\sigma^2(Fo^2)+(xP)^2$, where $P=(Fo^2+2Fc^2)/3$.

Table S3. The crystal data of 1,1,6,6-Tetraphenyl-2,4-hexadiyne-1,6-diol : 2(2(1H)-pyridone) (**I-c**).

$C_{30}H_{22}O_2 \cdot 2(C_5H_5NO)$	**start**	**Irrad. 1hr**	**Irrad. 2hr**	**Irrad. 3hr**	**Irrad. 4hr**
Temperature (K)	293	293	293	293	293
Formula weight	604.68	604.68	604.68	604.68	604.68
Crystal colour	colourless	colourless	colourless	colourless	colourless
Crystal size (mm)	0.30x0.20x0.01	0.30x0.20x0.01	0.30x0.20x0.01	0.30x0.20x0.01	0.30x0.20x0.01
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	*P-1*	*P-1*	*P-1*	*P-1*	*P-1*
Unit cell dimensions (Å), (°)					
a =	7.795 (2)	7.800 (1)	7.787 (1)	7.780 (1)	7.775 (1)
b =	8.071 (2)	8.081 (1)	8.065 (1)	8.059 (1)	8.058 (1)
c =	13.457 (3)	13.476 (2)	13.452 (2)	13.452 (2)	13.462 (2)
α =	85.12 (2)	85.03 (2)	85.02 (2)	84.98 (2)	84.97 (2)
β =	75.70 (2)	75.62 (2)	75.61 (2)	75.61 (2)	75.54 (2)
γ =	81.12 (3)	81.09 (2)	81.18 (2)	81.22 (2)	81.31 (2)
Volume (Å^3)	809.6 (3)	811.9 (2)	807.6 (2)	806.3 (2)	806.2 (2)
Z	1	1	1	1	1
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Wavelength MoKα, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.08	0.08	0.08	0.08	0.08
2θ max (°)	49.4	49.4	50.0	50.0	50.0
Min./Max. indices h,k,l	0/9,-9/9,-15/15	0/9,-9/9,-15/15	-9/8,-9/9,-14/15	0/9,-9/9,-15/16	0/9,-9/9,-15/16
Reflections collected/unique	6417 / 2727	6455 / 2720	6601 / 2805	8170 / 2840	8754 / 2842
R_{int}	0.045	0.055	0.060	0.052	0.052
Observed reflections (I>2σ(I))	1802	1713	1929	1949	1983
Data/parameters/restrains	2727 / 208 / 0	2720 / 209 / 0	2805 / 225 / 0	2840 / 225 / 0	2842 / 225 / 0
Goodness of fit on F^2	1.05	0.94	0.92	0.91	0/90
Final R_1 indices (I>2σ(I))	0.046	0.047	0.047	0.046	0.046
wR_2 indices	0.123	0.123	0.132	0.127	0.131
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0. 17, -0.13	0. 15, -0.15	0. 18, -0.16	0. 14, -0.17	0. 20, -0.21
Weighting scheme: x; y[a]	0.0624 / 0.0	0.0657 / 0.0	0.0759 / 0.0578	0.0707 / 0.1483	0.0773 / 0.1943
Extinction coefficient	-	-	-	-	-

[a] $w = 1/[(\sigma^2(Fo^2)+(xP)^2 + yP]$, where $P=(Fo^2+2Fc^2)/3$.

Table S3. (cont.)

$C_{30}H_{22}O_2 \cdot 2(C_5H_5NO)$	**Irrad. 5hr**	**Irrad. 6hr**	**Irrad. 7hr**	**Irrad. 17hr**	**Irrad. 27hr**
Temperature (K)	293	293	293	293	293
Formula weight	604.68	604.68	604.68	604.68	604.68
Crystal colour	colourless	colourless	colourless	colourless	colourless
Crystal size (mm)	0.30x0.20x0.01	0.30x0.20x0.01	0.30x0.20x0.01	0.30x0.20x0.01	0.30x0.20x0.01
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	*P-1*	*P-1*	*P-1*	*P-1*	*P-1*
Unit cell dimensions (Å), (°)					
a =	7.769 (1)	7.773 (1)	7.770 (1)	7.744 (1)	7.809 (1)
b =	8.054 (1)	8.057 (1)	8.055 (1)	7.992 (2)	7.861 (2)
c =	13.456 (2)	13.470 (2)	13.474 (2)	13.534 (3)	13.539 (3)
α =	84.98 (2)	84.97 (2)	84.99 (2)	85.40 (2)	87.33 (2)
β =	75.56 (2)	75.51 (2)	75.45 (2)	75.41 (2)	75.75 (2)
γ =	81.35 (3)	81.44 (2)	81.50 (2)	82.78 (2)	84.88 (2)
Volume (Å^3)	805.0 (2)	806.5 (2)	806.2 (2)	803.2 (3)	802.1 (3)
Z	1	1	1	1	1
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Wavelength MoKα, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.08	0.08	0.08	0.08	0.08
2θ max (°)	50.0	50.0	50.0	50.0	50.0
Min./Max. indices h,k,l	0/9,-9/9,-15/16	0/9,-9/9,-15/16	0/9,-9/9,-15/16	0/9,-9/9,-15/16	0/9,-9/9,-15/16
Reflections collected/unique	8470 / 2837	8558 / 2841	7936 / 2836	8467 / 2822	8031 / 2790
R_{int}	0.062	0.064	0.054	0.075	0.078
Observed reflections (I>2σ(I))	1863	1838	1952	1617	1488
Data/parameters/restrains	2837 / 225 / 0	2841 / 225 / 0	2836 / 225 / 0	2822 / 225 / 0	2790 / 225 / 0
Goodness of fit on F^2	0.89	0.99	0.92	1.01	0.92
Final R_1 indices (I>2σ(I))	0.048	0.049	0.047	0.064	0.065
wR_2 indices	0.139	0.138	0.132	0.216	0.192
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0.18, -0.21	0.26, -0.20	0.30, -0.25	0.24, -0.22	0.23, -0.21
Weighting scheme: x; y[a]	0.0797 / 0.1907	0.0693 / 0.1277	0.0886 / 0.3286	0.1347 / 0.0	0.1073 / 0.0
Extinction coefficient	-	-	-	-	-

Table S3. (cont.)

$C_{30}H_{22}O_2 \cdot 2(C_5H_5NO)$	**Irrad. 40hr**	**Irrad. 60hr**	**Irrad. 80hr**
Temperature (K)	293	293	293
Formula weight	604.68	604.68	604.68
Crystal colour	colourless	colourless	colourless
Crystal size (mm)	0.30x0.20x0.01	0.30x0.20x0.01	0.30x0.20x0.01
Crystal system	triclinic	triclinic	triclinic
Space group	*P-1*	*P-1*	*P-1*
Unit cell dimensions (Å), (°)			
a =	7.743 (1)	7.740 (1)	7.781 (1)
b =	7.751 (2)	7.780 (2)	7.803 (2)
c =	13.459 (3)	13.527 (3)	13.491 (3)
α =	87.69 (2)	87.86 (2)	87.76 (2)
β =	76.13 (2)	76.29 (2)	76.74 (2)
γ =	85.27 (2)	85.79 (2)	86.24 (2)
Volume (Å^3)	781.4 (3)	789.1 (3)	795.3 (3)
Z	1	1	1
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Wavelength MoKα, λ (Å)	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.08	0.08	0.08
2θ max (°)	50.0	50.0	50.0
Min./Max. indices h,k,l	0/9,-9/9,-15/16	0/9,-9/9,-15/16	0/9,-9/9,-15/16
Reflections collected/unique	7220 / 2660	7650 / 2767	7657 / 2784
R_{int}	0.066	0.086	0.083
Observed reflections (I>2σ(I))	1727	1428	1433
Data/parameters/restrains	2660 / 225 / 0	2767 / 225 / 0	2784 / 225 / 0
Goodness of fit on F^2	0.97	0.76	0.84
Final R_1 indices (I>2σ(I))	0.066	0.054	0.056
wR_2 indices	0.206	0.150	0.138
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0.33, -0.22	0.22, -0.17	0.22, -0.16
Weighting scheme: x; y[a]	0.1400 / 0.0389	0.095 / 0.0	0.0646 / 0.0
Extinction coefficient	-	-	-

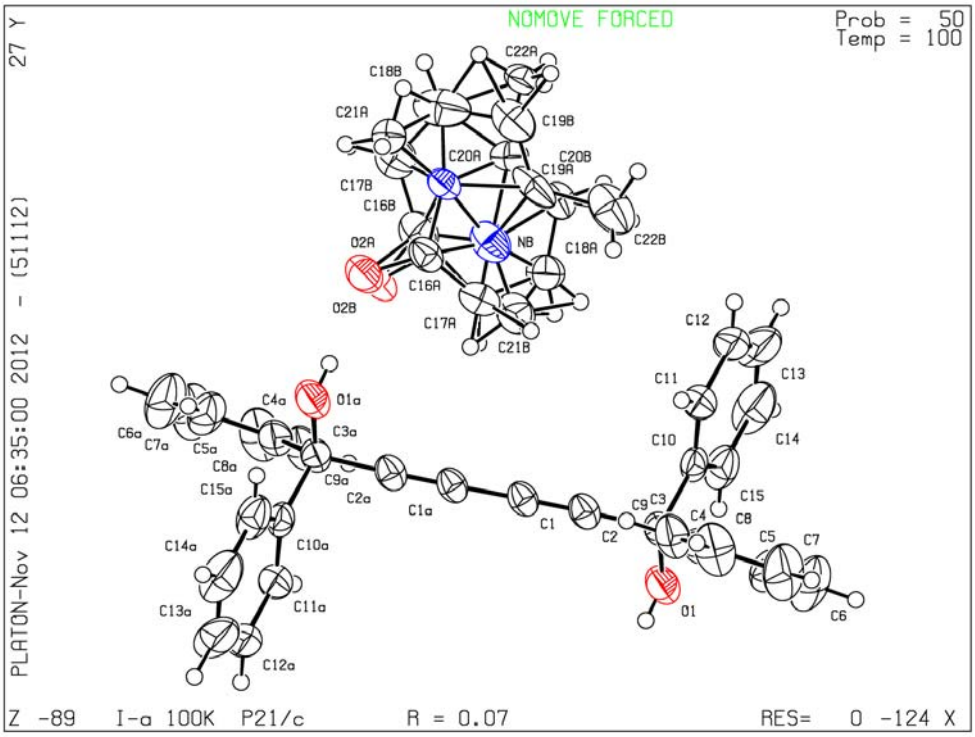

Figure S1 (I-a) before irradiation

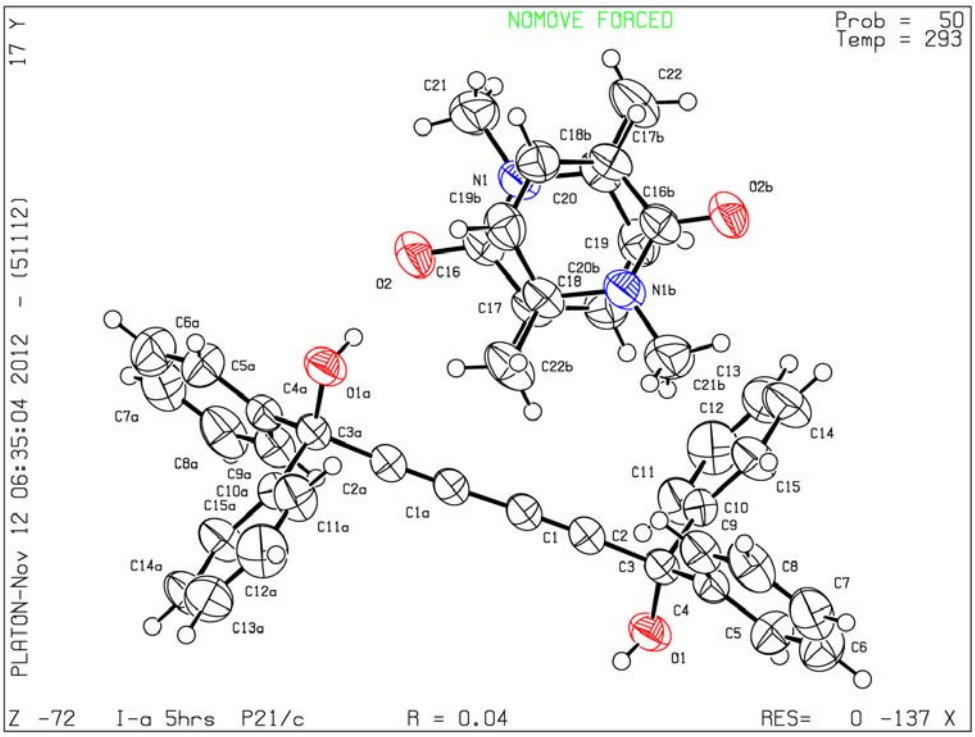

Figure S2 (I-a) after irradiation to full conversion

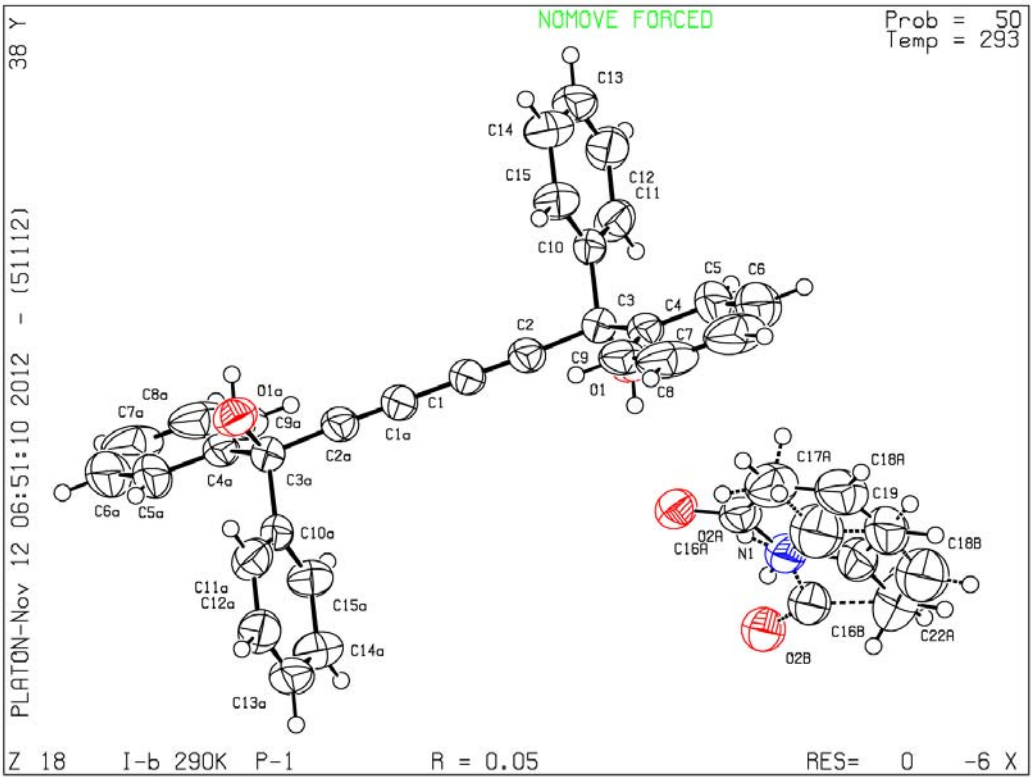

Figure S3. The structure of I-b at 290K.

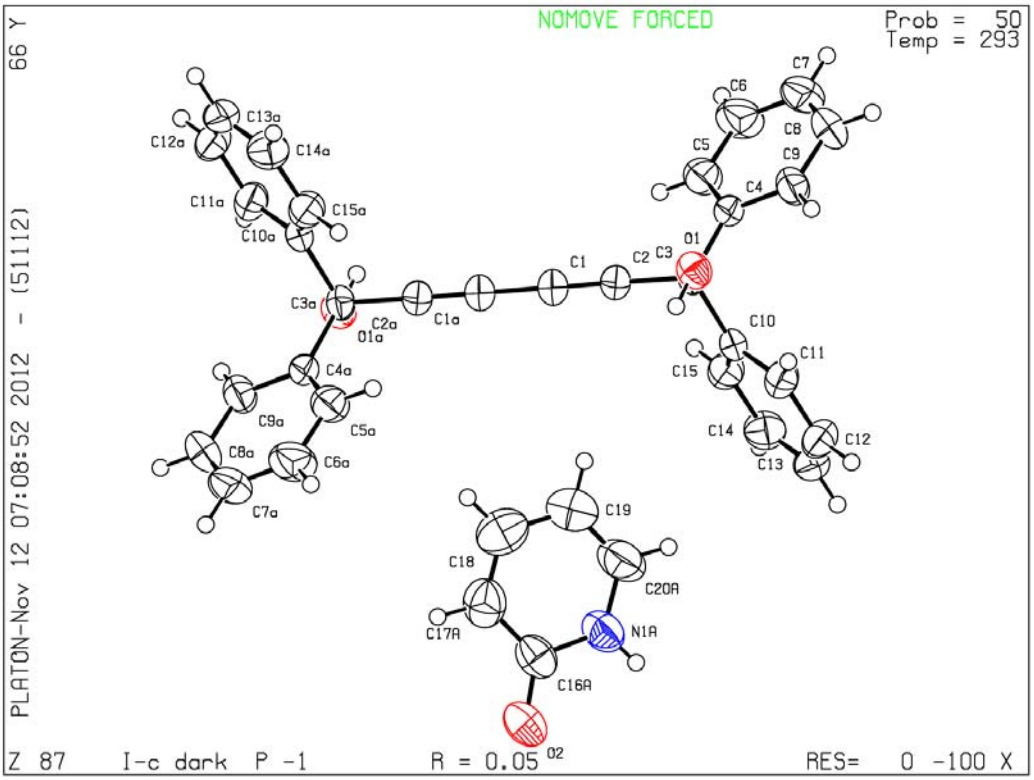

Figure S4. The structure of I-c before irradiation

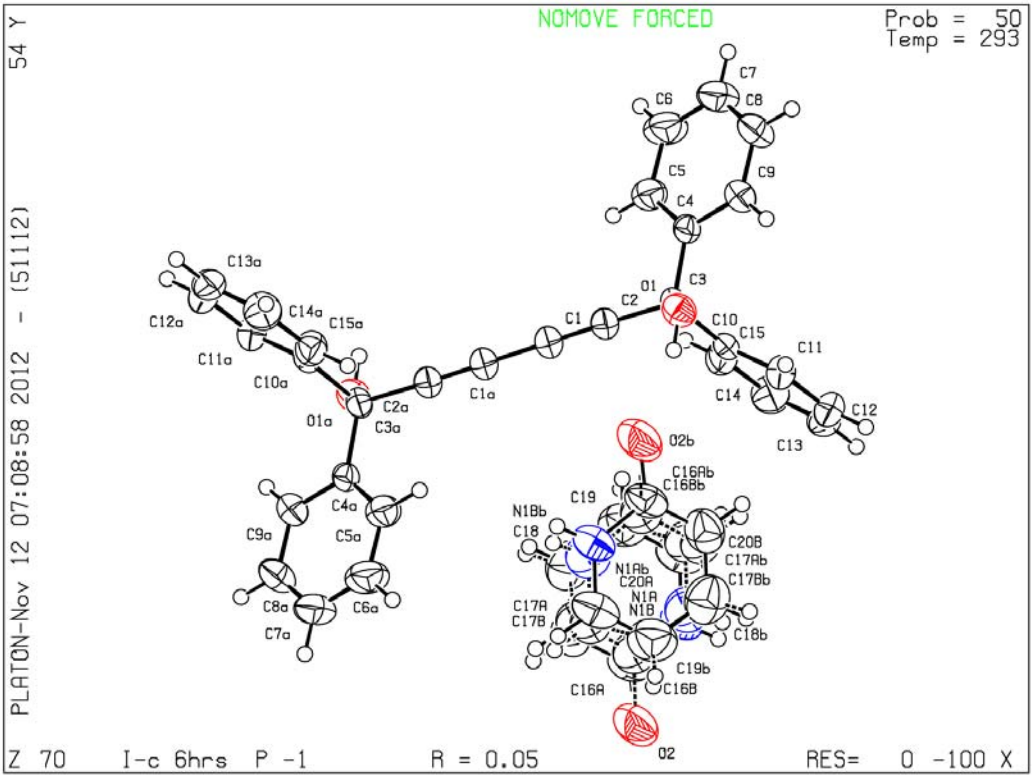

Figure S5. The structure of I-c after 6hrs of irradiation