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Supplementary information

Visible light induced degradation of pollutant dye using self-assembled graphene oxide-molybdenum oxo-bis(dithiolene) ($[Ph_4P]_2[MoO(S_2C_2(CN)_2)_2]$) composite

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Supporting information

S-1: UV-Vis study of 1 and washed composite

The reaction of oxo-molybdenum(IV)(bis-dithiolene) complex $[Ph_4P]_2[MoO(S_2C_2(CN)_2)_2]$, **1** with GO during composite synthesis might involve some oxo-transfer from GO to **1** to yield its oxidized form dioxo-molybdenum(VI)(bis-dithiolene) complex $[Ph_4P]_2[MoO_2(S_2C_2(CN)_2)_2]$. This species has been abbreviated as ***dioxo*** in the manuscript/supporting information. The oxidation state of Mo will change from +4 in **1** to +6 in ***dioxo*** and could be easily be identified by UV-vis spectrum and XPS. To identify the formation of such ***dioxo*** species, if any, in course of the composite formation, we have recorded the absorbance spectrum of standard samples of **1** as well as ***dioxo***. Figure S1 show the UV-visible spectra of **1**, ***dioxo*** and the washed part (red circle part in Fig 1d; main text) of the as synthesized **GO-Mo** composite in acetonitrile solvent. Compound **1** (black color graph, Figure S1) shows peak at 366 nm.[1] The ***dioxo*** (red color graph, Figure S1) show peak at 366, 428 and broad shoulder at 534 nm.[1] The blue color spectrum (Figure S1) corresponds to the washed part of as synthesized **GO-Mo** with peaks at 366 nm, reveals absence of Mo+6 within the detection limit of the concentration by absorption spectroscopy. This attests to the fact that almost no oxo-transfer reaction took place between the GO and **1** during composite synthesis under our experimental conditions. XPS analysis also shows Mo (+4) in the composite (see Figure 3d and S3).

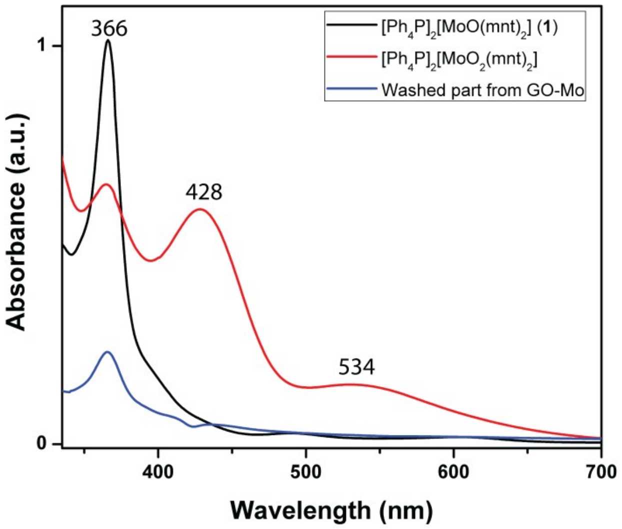


Figure S1: UV-vis spectra of **1** (black), standard $[Ph_4P]_2[MoO_2(mnt)_2]$ (red) and washed part of as synthesized **GO-Mo** (blue)

S-2: SEM, TEM and Raman spectrum of GO

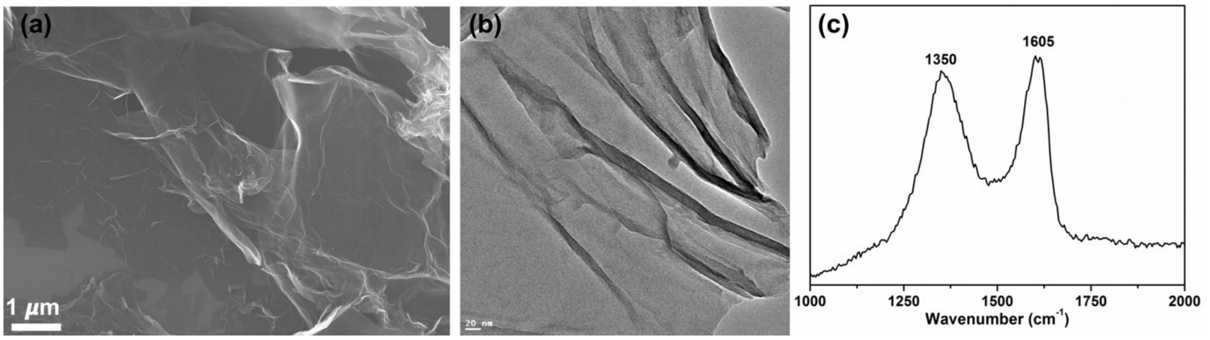


Figure S2: (a) SEM (b) TEM image of GO (c) Raman spectrum of GO.

S-3: Effect of concentration of 1 $[Ph_4P]_2[MoO(S_2C_2(CN)_2)_2]$

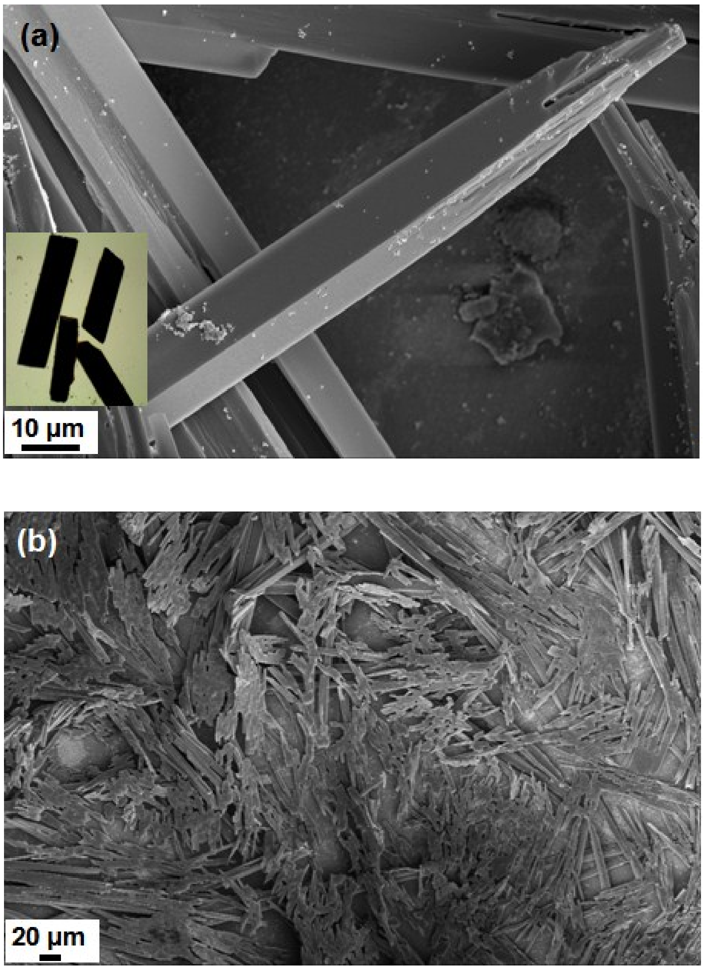


Figure S-3: FESEM images for (a) the crystallization of **1** over *π*–surface of GO when used in low concentration (5 mg/3 mL). Optical image of single crystal of **1** is shown in inset; (b) Partial synthesis of layered **GO-Mo** as scaffold structure at concentration of 20 mg/3 mL. Acetonitrile is used as the solvent for **1**.

S-4: XPS spectra of complex *1*, GO-Mo and GO

Figure S3a and S3b show the survey, S2p and P2p of **1** and **GO-Mo** respectively. The peak for S2p and P2p in **GO-Mo** were shifted to higher binding energy by 0.9 and 0.5 eV respectively as compared to **1**. The shift to higher binding energy corresponds to the change in chemical environment due to the non-covalent interactions between **1** and GO.[2] Figure S3c shows the survey, O1s and C1s of GO. The survey spectrum shows the peak only for carbon and oxygen. The absence of any peak in the range of 640-642 eV suggests that GO is free from Mn ion. The C1s of GO show a peak at 284.6 eV correspond to sp^2 carbon and a broad peak centred at 286.8 eV is an overlap peak for C–O, C=O and O–C=O groups (sp^3 carbon).[3]

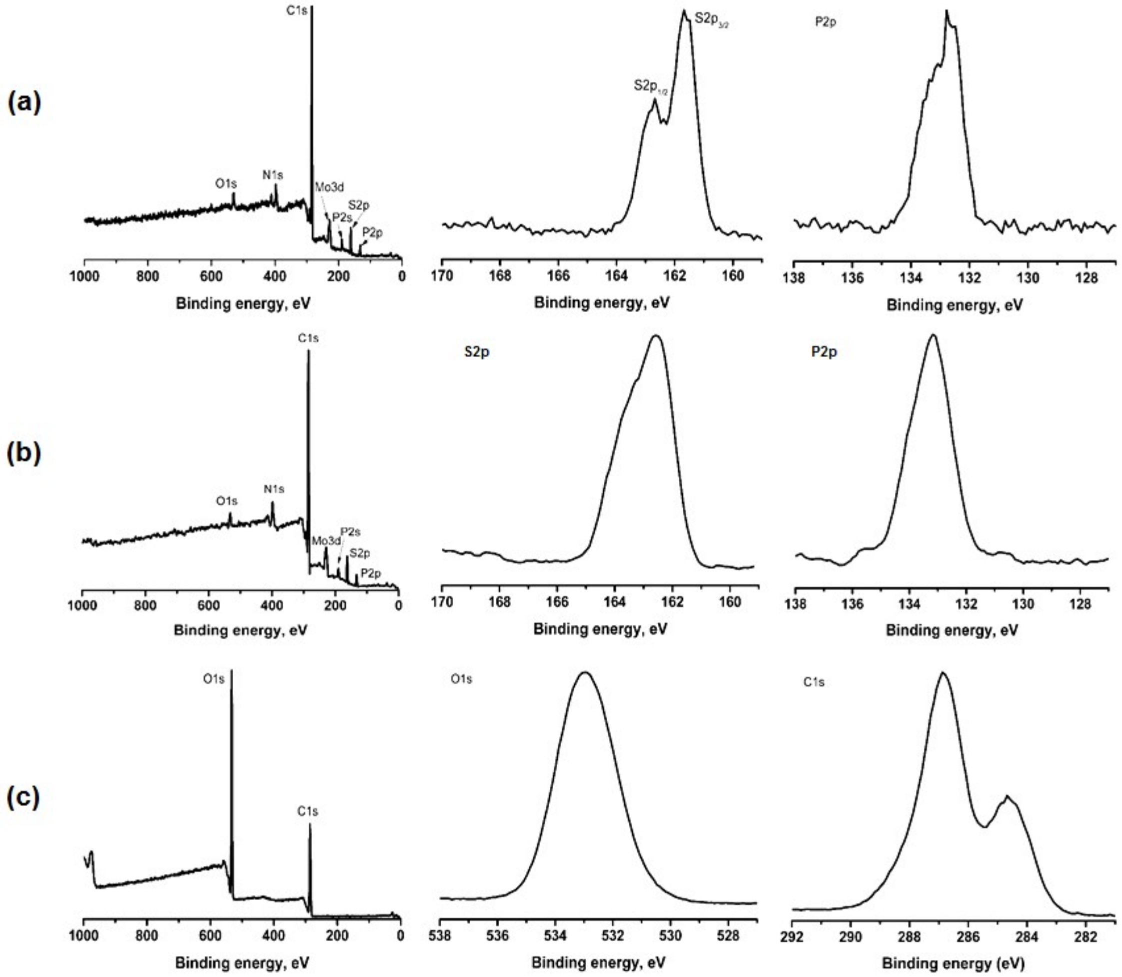


Figure S-4: XPS spectra of (a) **1**: survey, S2p, P2p; (b) **GO-Mo**: survey, S2p, P2p; (c) GO: survey, O1s, C1s. (from left to right)

S-5: Dye degradation study

10 ppm aqueous solutions of Rhodamine B (RhB) and Rose Bengal (RB) dyes were used for the study. Briefly, the dye solutions (with and without **GO-Mo**) in a pyrex glass bottle with teflon lid was covered with a water circulation jacket. The temperature of water jacket is maintained ~20 °C. A 100 W tungsten bulb (Philips, India) was used as a visible light source.

The dye solution with a known amount of **GO-Mo** was allowed to stir for 5 min to equilibrate the mixture (in dark) followed by its exposure to visible light. 2 mL of the dye solution was taken out at particular time intervals and centrifuged at 5000 rpm. The supernatant was transferred to a clean "PerkinElmer" quartz cell (10 mm path length) to record UV-Vis spectrum. The change in the absorption intensity at 540 and 553 nm for RB and RhB, respectively were monitored by UV-Vis absorbance over the period of time as a measure of dye degradation. Furthermore, the kinetics of RhB and RB dye degradation reactions were performed with **GO-Mo** and for RhB (chosen as representative xanthine dye) with treated **GO-Mo**. Following control experiments: (a) visible light irradiation of only dye solution, (b) dye solution with only GO, and (c) dye solution with **GO-Mo** in dark; for 30 min were also performed and changes in the absorbance at chosen wavelength were recorded (Table S-5).

Table S-5: Dye degradation control experiments

Dye	Study conditions (catalyst/visible light etc.)	Time (in min)	Change in dye concentration upon visible light irradiation (%)
RhB	Dye only, under visible light irradiation	30	1.0
RB			2.5
RhB	Dye + **1**, under visible light irradiation	30	2
RB			1.7
RhB	Dye + GO, under visible light irradiation	30	5
RB			7
RhB	Dye + GO-Mo, under dark	30	5-7
RB			

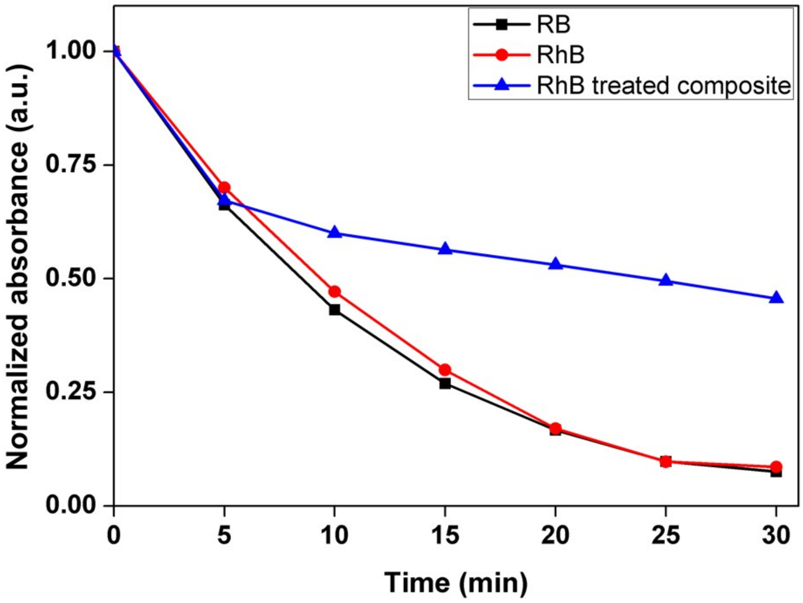


Figure S-5: Normalized UV-Vis spectrum of RB, RhB with GO-Mo and RhB with treated composite.

S-6: Characterization of GO-Mo composite

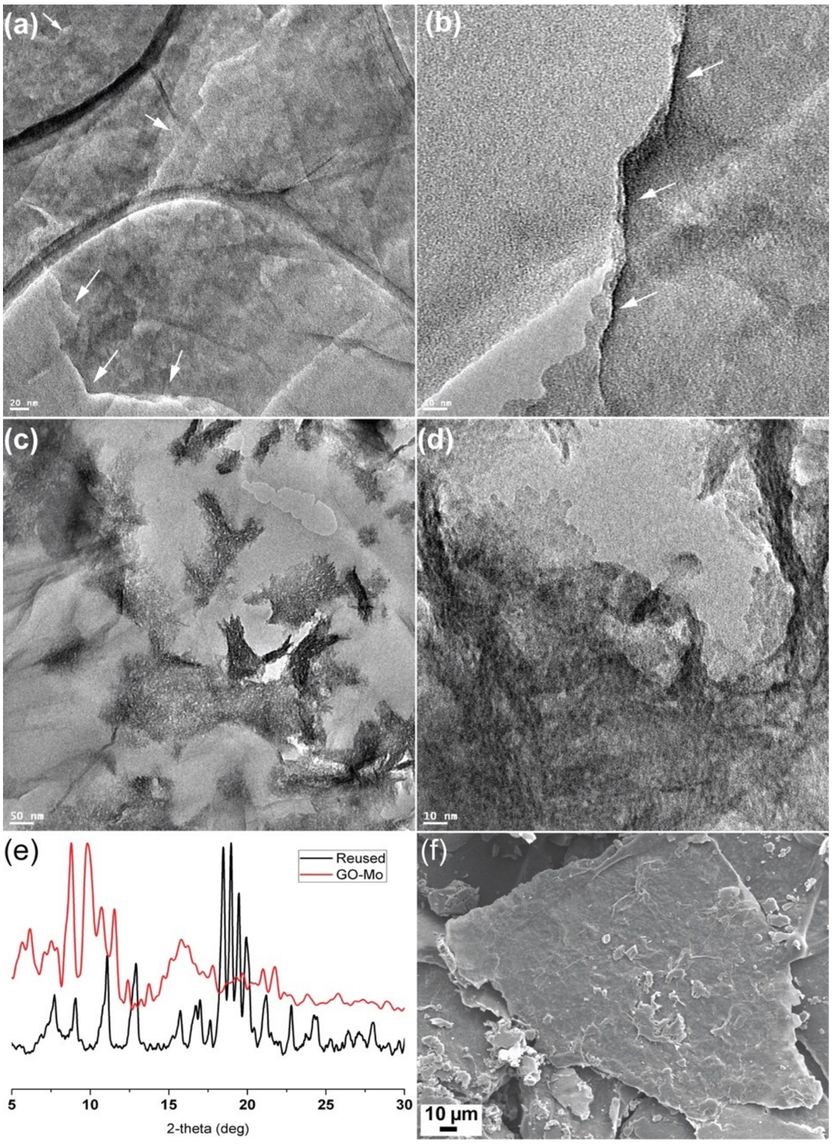


Figure S-6: TEM image of **GO-Mo** (a, b) as synthesized (c, d) after 5 cycle of use (e) Comparitive PXRD of as synthesized **GO-MO** and after 5 cycle of use (f) SEM image of used **GO-Mo** composite.

S-7: *Treated composite*: reactivation of used GO-Mo by ethanol

The used **GO-Mo** composite (after 5th cycle) was sonicated with 1 mL absolute ethanol for ~20 min. The solution was centrifuged and supernatant was discarded. The **GO-Mo** composite was washed with deionized water. After washing, the composite was dried under vacuum ($< 2\times10^{-3}$ Torr) at 40 °C for overnight. The dried treated **GO-Mo** composite was used for dye-degradation under light exposure for a total of 90 mins as described in S-4.

S-8: Mass spectrum of degraded dye

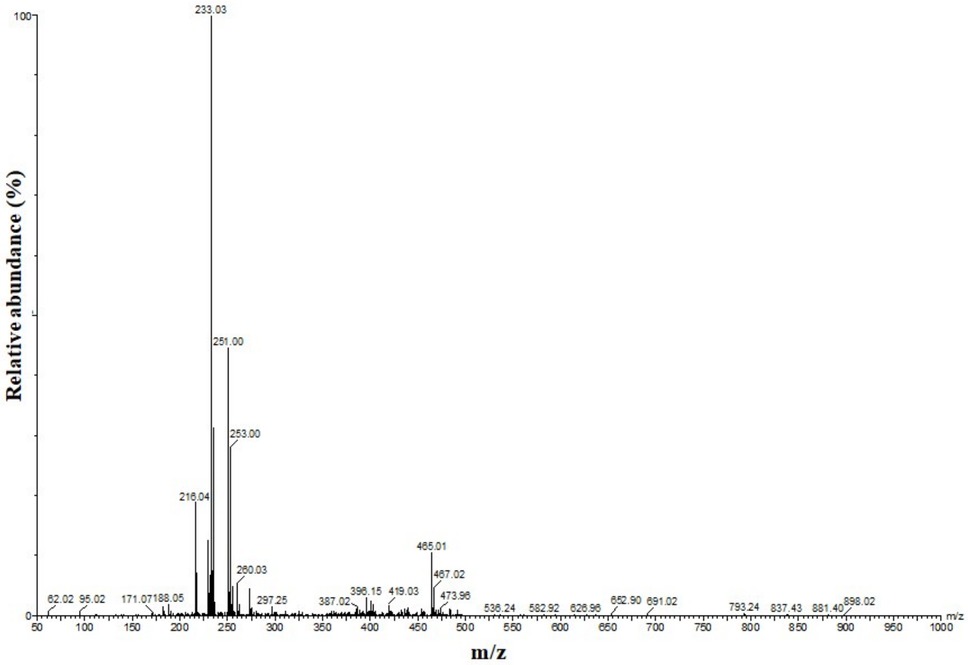
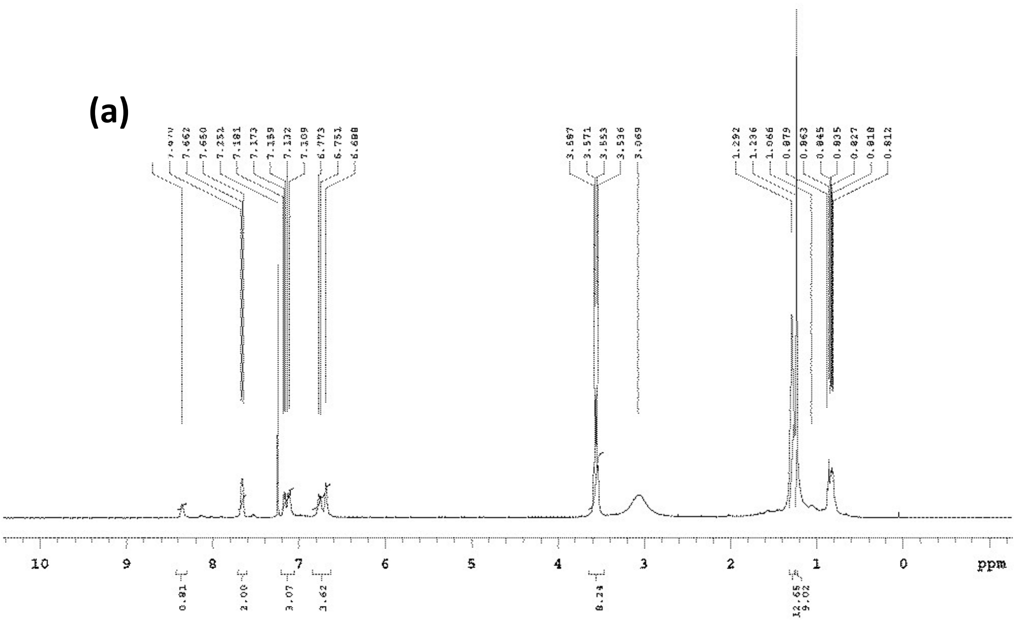


Figure S-8: Mass spectrum of degraded RB dye solutions over **GO-Mo** composite after 30 min under visible light illumination.

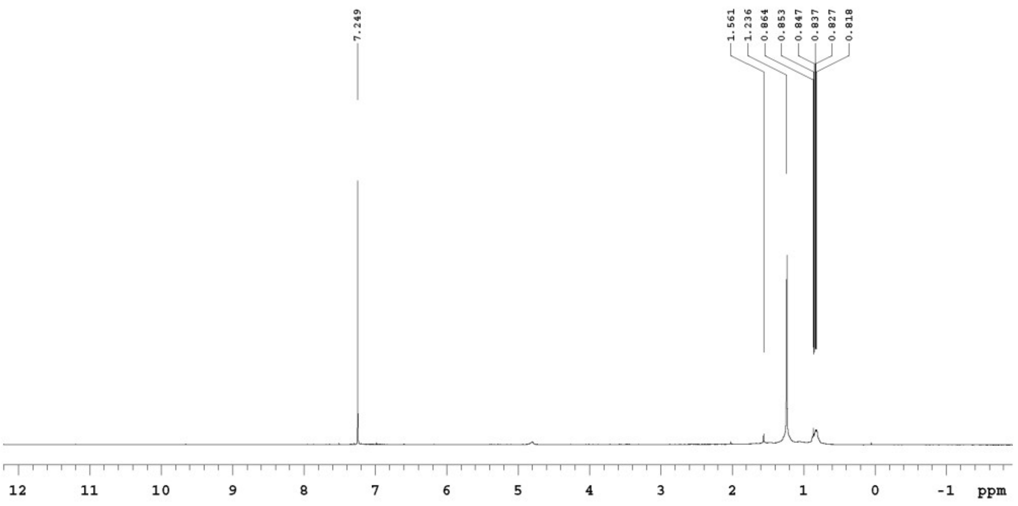
S-9: Full range ^{1}H NMR spectra of (a) RB dye, (b) Photodegraded RB dye.

(a)



PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 3.722 sec Width 8802.8 Hz 16 repetitions	OBSERVE H1, 399.8257242	DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 1 minute		RHB-1H Solvent: cdcl3 Ambient temperature Operator: vnmr1 File: RHB-1H VNMRS-400 "Agilent-NMR"

(b)



PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 3.722 sec Width 8802.8 Hz 32 repetitions	OBSERVE H1, 399.8257242	DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 2 minutes		Dyedg-1H Solvent: cdcl3 Ambient temperature Operator: vnmr1 VNMRS-400 "Agilent-NMR"

Reference

1. S. K. Das, P. K. Chaudhury, D. Biswas and S. Sarkar, *J. Am. Chem. Soc.*, 1994, **116**, 9061-9070.
2. J. S. Stevens, L. K. Newton, C. Jaye, C. A. Muryn, D. A. Fischer and S. L. M. Schroeder, *Cryst. Growth Des.*, 2015, **15**, 1776-1783.
3. Z. Wang, Y. Dong, H. Li, Z. Zhao, H. Bin Wu, C. Hao, S. Liu, J. Qiu and X. W. Lou, *Nat. Commun.*, 2014, **5**, 5002.