

Tunable and Wavelength-Gated Reversible Photopolymerization of Quinolinone-Based Telechelic Oligomers via $[2\pi+2\pi]$ Cycloaddition

Logan Charton,¹ Richard Remy,² Céline Calvino^{1,2*}

¹ L. Charton, C. Calvino

University of Freiburg – Department of Microsystems Engineering (IMTEK)

Georges-Köhler-Allee 102, D-79110 Freiburg, Germany

E-mail: Celine.calvino@livmats.uni-freiburg.de

² R. Remy, C. Calvino

Cluster of Excellence livMatS, University of Freiburg (livMatS)

FIT-Freiburg Center for Interactive Materials and Bioinspired Technologies

Georges-Köhler-Allee 105, D-79110 Freiburg, Germany

E-mail: Celine.calvino@livmats.uni-freiburg.de

Table of Contents:

1	Supporting Data	S-2
2	Supporting Experimental Section	S-11
3	References	S-36

1 Supporting Data

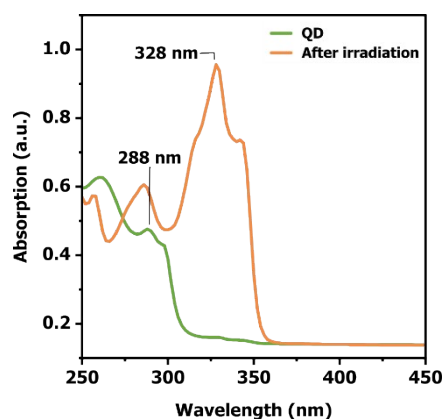


Figure S1. UV-vis absorption spectra of neat **QD** (green) and **QD** after 2 min of irradiation at 265 nm under oxygen-free conditions (orange). Photoreaction was carried out in acetonitrile (ACN) at $c = 3 \times 10^{-5} \text{ mol L}^{-1}$ and irradiated with an LED photoreactor operating at a power of 22 mW.

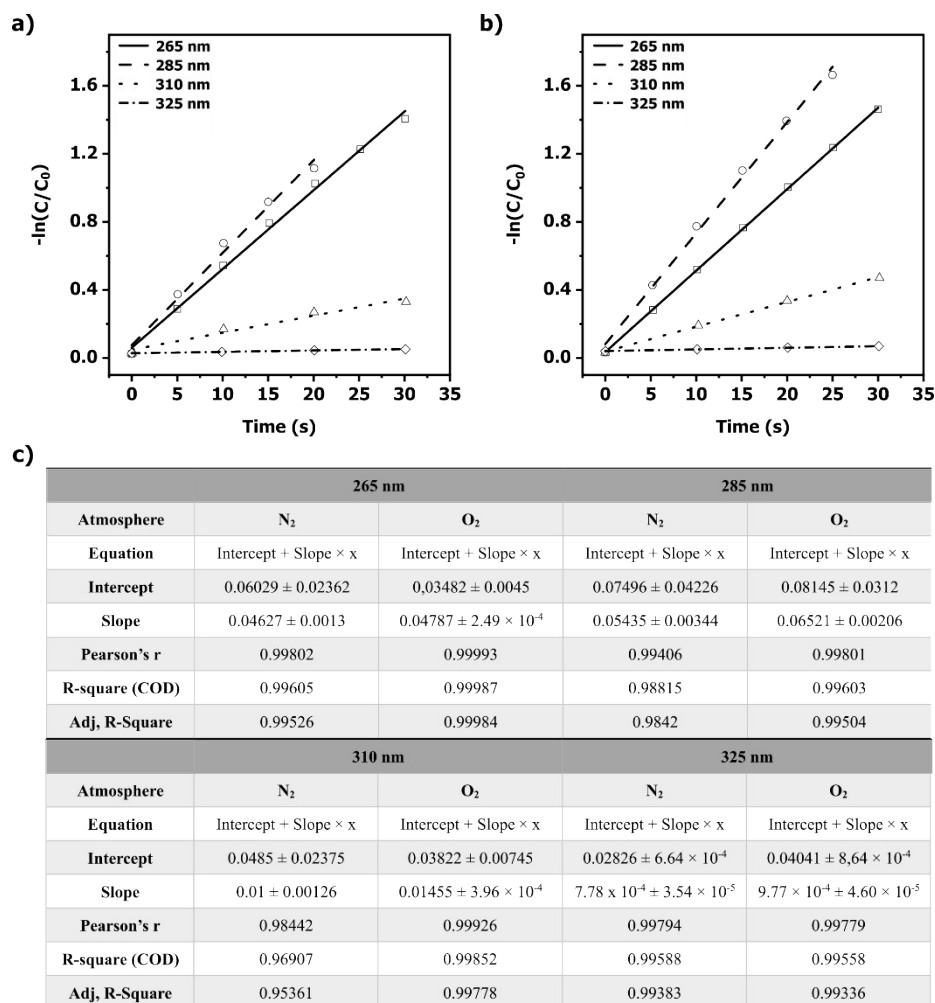


Figure S2. a) Cycloreversion kinetic profiles of **QD** in ACN solutions ($c = 3 \times 10^{-5} \text{ mol L}^{-1}$) upon irradiation at 265, 285, 310, and 325 nm under oxygen-free conditions, b) and under oxygenated conditions. c) Table representing the first-order linear equations defining the kinetics obtained in (a) and (b). Photoreactions were conducted with an LED photoreactor operating at power levels ranging from 22 to 80 mW.

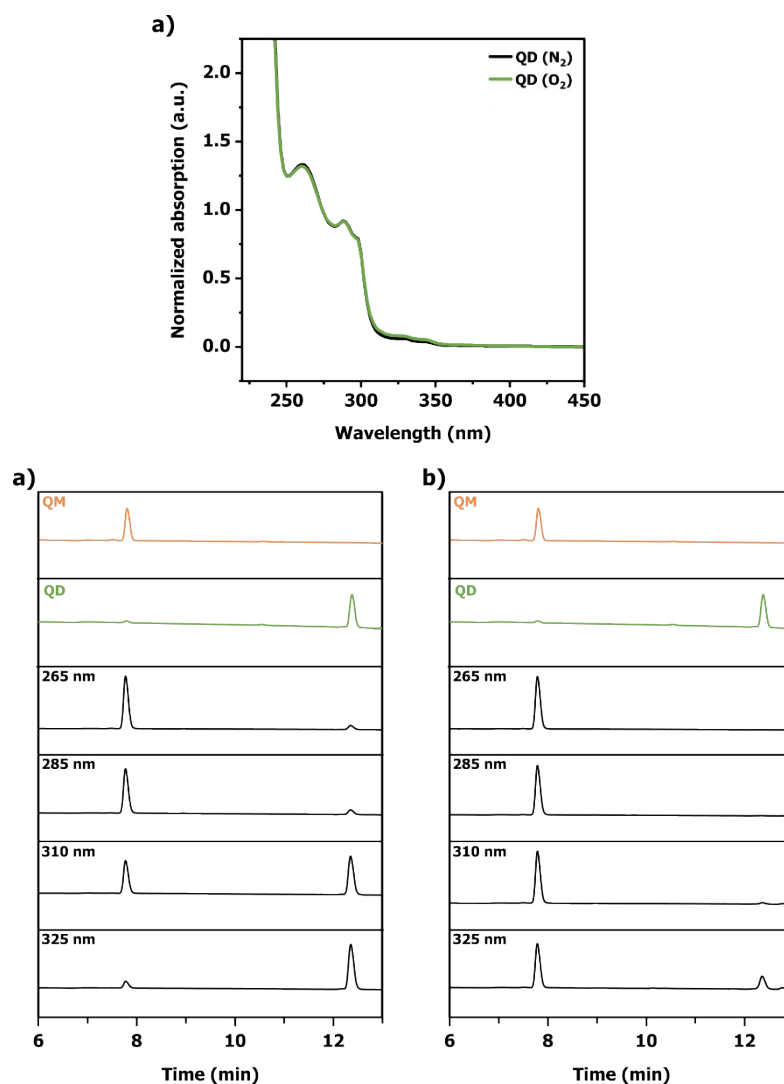


Figure S3. a) UV-vis spectra of QD solutions in nitrogen-purged ACN (black) and in ambient-air-saturated ACN (green), normalized at 274 nm. b) Comparison of HPLC chromatograms of QD (green), QM (orange), and QD after irradiation at 265, 285, 310, and 325 nm under oxygen-free conditions; c) corresponding chromatograms obtained under oxygenated conditions. Each chromatogram corresponds to a measurement taken at the plateau value of the irradiation time range (1.5–50 min), as shown in Figure 2b–c. Photoreactions were conducted in ACN solutions at $c = 3 \times 10^{-5} \text{ mol L}^{-1}$ and irradiated with an LED photoreactor operating at power levels ranging from 22 to 80 mW.

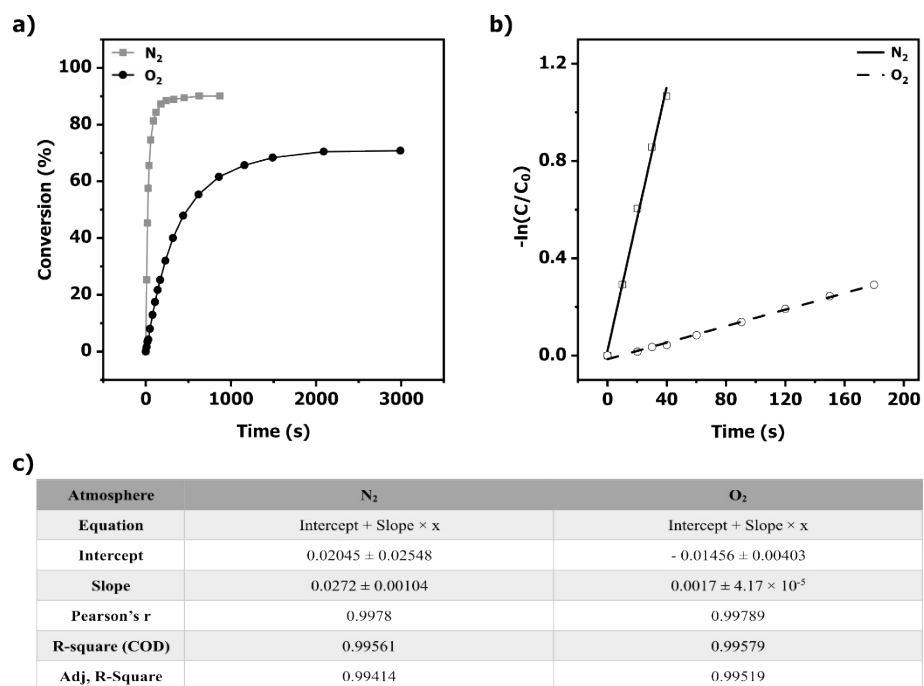


Figure S4. a) Comparison of the photocycloaddition reaction rates of **QM** solutions under oxygen-free conditions (grey) and in the presence of trace amounts of oxygen (black) after irradiation at 340 nm, b) and their corresponding kinetic profiles. c) Table representing the first-order linear equations describing the kinetics obtained in (b). Photoreactions were conducted in ACN solutions at $c = 6 \times 10^{-5} \text{ mol L}^{-1}$ and irradiated with an LED photoreactor operating at a power of 33 mW.

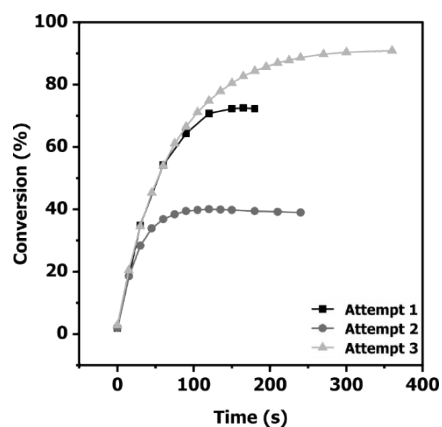


Figure S5. Comparison of the photocycloreversion conversions of **QD** solutions at 310 nm under oxygenated conditions, prepared from an oxygenated stock solution in a nitrogen glovebox (**attempt 1**), prepared one day later from the same stock solution, also in a nitrogen glovebox (**attempt 2**), and prepared under ambient conditions (**attempt 3**). Photoreactions were carried out in ACN solutions at $c = 3 \times 10^{-5} \text{ mol L}^{-1}$ and irradiated with an LED photoreactor operating at a power of 80 mW.

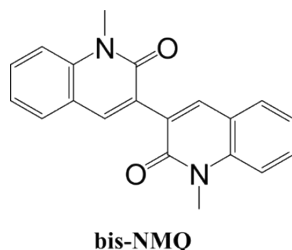


Figure S6. Structure of Bis-N-Methyl-Quinolinone (**bis-NMQ**), a possible side-product formed during irradiation of quinolinone dimers in the presence of oxygen, as previously reported in the literature.¹

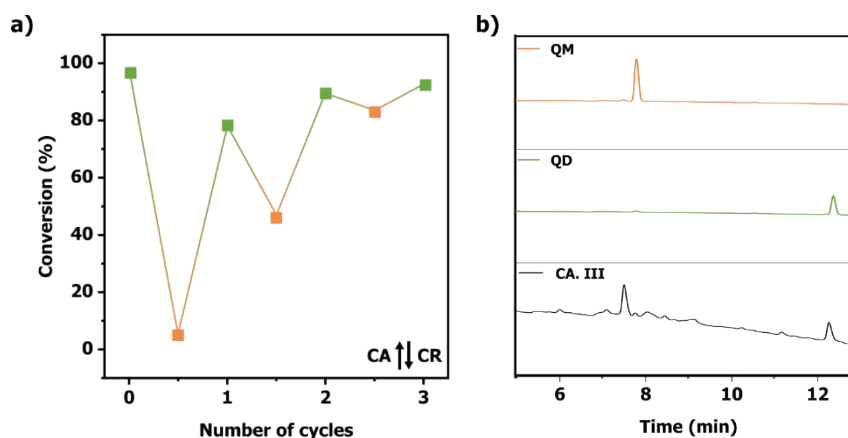


Figure S7. a) Subsequent irradiation cycles of **QD** conducted under ambient atmosphere at 265 nm for the cycloreversion (CR, from green to orange) and at 340 nm for the cycloaddition (CA, from orange to green). **b)** Comparison of HPLC chromatograms for **QM** (orange), **QD** (green), and the resulting product mixture obtained after three irradiation cycles (CA. III, black). Photoreactions were conducted in ACN solutions at $c = 3 \times 10^{-5} \text{ mol L}^{-1}$ and irradiated with an LED photoreactor operating at power levels ranging from 22 to 33 mW.

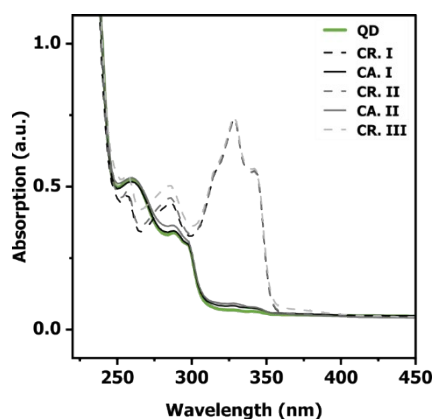


Figure S8. UV-vis absorption spectra of **QD** (green), and of the subsequent irradiation cycles of **QD** conducted at 310 nm under oxygenated conditions for the cycloreversion (CR.I to III) and at 340 nm under oxygen-free conditions for the cycloaddition (CA.I to II). Photoreactions were carried out in ACN solutions at $c = 3 \times 10^{-5} \text{ mol L}^{-1}$ and irradiated with an LED photoreactor operating at power levels ranging from 33 to 80 mW.

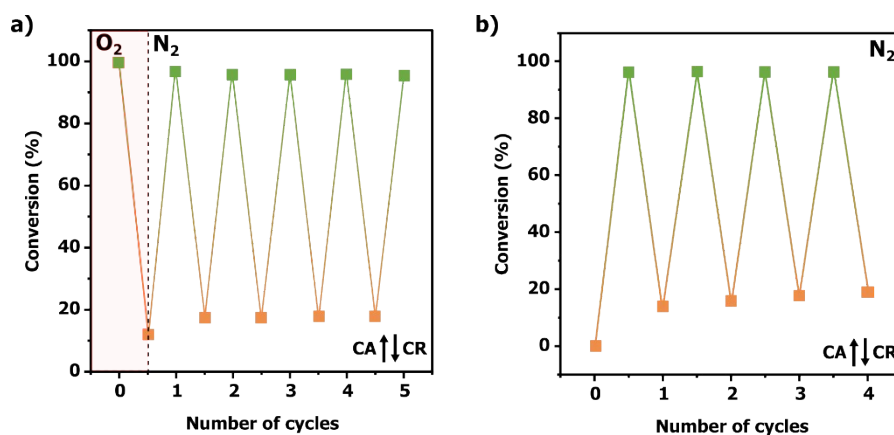


Figure S9. **a)** Subsequent irradiation cycles of **QM** solution in ACN ($c = 6 \times 10^{-5} \text{ mol L}^{-1}$) at 340 nm for the cycloaddition (CA, from orange to green), and 265 nm for the cycloreversion (CR, from green to orange), under oxygen-free conditions, after an initial cycloreversion of a **QD** solution in ACN ($c = 3 \times 10^{-5} \text{ mol L}^{-1}$) at 310 nm under oxygenated conditions. **b)** Subsequent irradiation cycles of **QM** solution in ACN ($c = 6 \times 10^{-5} \text{ mol L}^{-1}$), at 340 nm for the cycloaddition (CA, from orange to green), and 265 nm for the cycloreversion (CR, from green to orange). The photoreactions were carried out in using an LED photoreactor operating at power levels ranging from 33 to 80 mW.

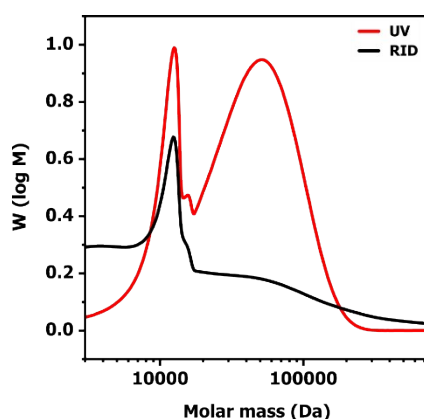


Figure S10. GPC chromatograms of **QM-PEG-QM** comparing the refractive index detector (RID) signal (black) and the UV detector signal (red).

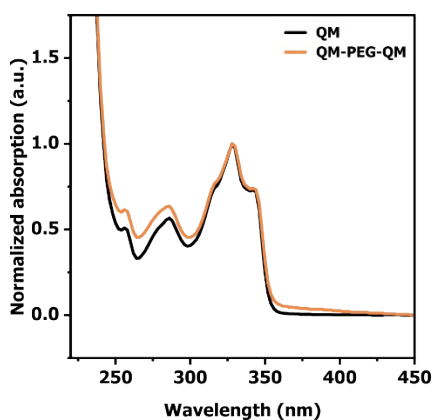


Figure S11. UV-vis absorption spectra of **QM** (black) and **QM-PEG-QM** (orange), normalized at 328 nm, in ACN solutions at $c \approx 10^{-5} \text{ mol L}^{-1}$.

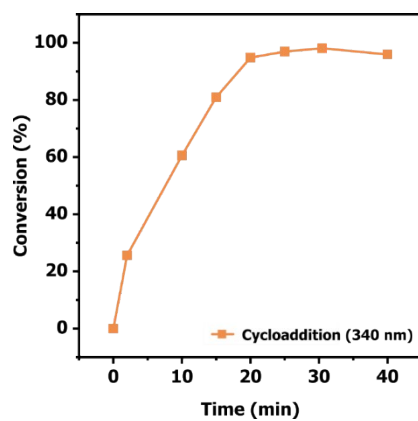


Figure S12. Conversion of **QM-PEG-QM** into **poly(PEG-QD)** as a function of irradiation time, demonstrating the photoextension of **QM-PEG-QM** via cycloaddition at 340 nm under oxygen-free conditions. The photoreaction was carried out in ACN at $c = 50 \text{ mg mL}^{-1}$ using an LED photoreactor operating at a power of 33 mW.

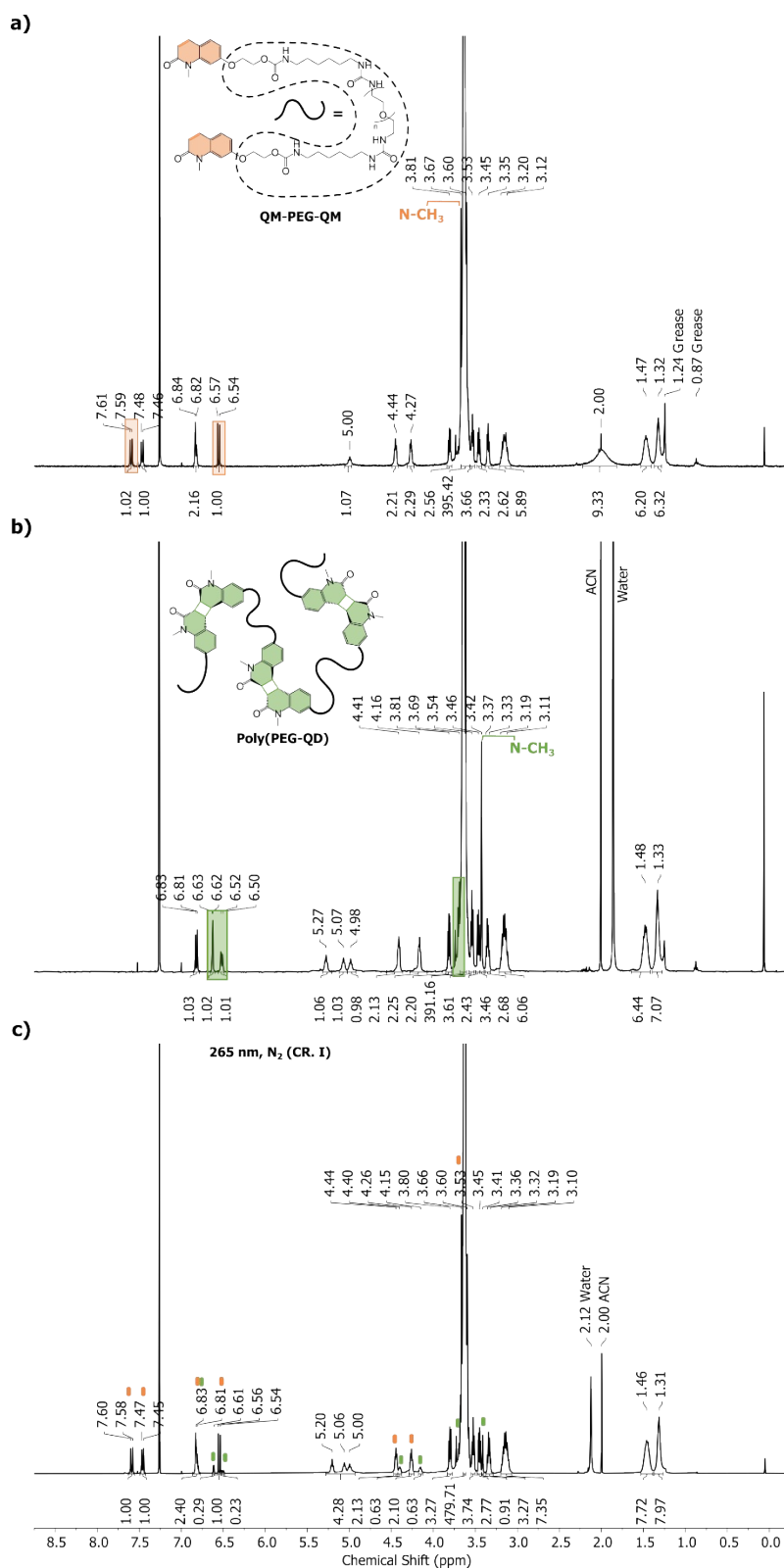


Figure S13. ¹H-NMR spectra in CDCl₃: **a)** QM-PEG-QM; **b)** Poly(PEG-QD), obtained after irradiation of QM-PEG-QM at $c = 50 \text{ mg mL}^{-1}$ in CAN, at 340 nm for 25 min under oxygen-free conditions; **c)** QM-PEG-QM obtained after irradiation of poly(PEG-QD) at $c = 50 \text{ mg mL}^{-1}$ in ACN, at 265 nm for 57 min under oxygen-free conditions (CR. I). **Poly(PEG-QD):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.83–6.81 (d, 1H, ArH), 6.63–6.62 (d, 1H, ArH), 6.52–6.50 (d, 1H, ArH), 5.27 (t, 1H, NH), 5.07 (t, 1H, NH), 4.98 (t, 1H, NH), 4.41 (t, 2H, CH₂-O(CO)), 4.16 (t, 2H, ArO-CH₂O), 3.81–3.42 (dt, O-¹³CH₂-CH₂-O), 3.69 (2H, cyclobutane-H), 3.64 (m, 391H, PEG-H), 3.54 (t, 2H, PEG-OCH₂-CH₂-NH), 3.42 (s, 3H, N-CH₃), 3.37 (t, 2H, PEG-OCH₂-CH₂-NH), 3.19–3.11 (m, 4H, CH₂-CH₂-NH(CO)), 1.48 (m, 4H, N(H)-CH₂-CH₂-CH₂), 1.33 (m, 4H, CH₂-CH₂-CH₂-CH₂).

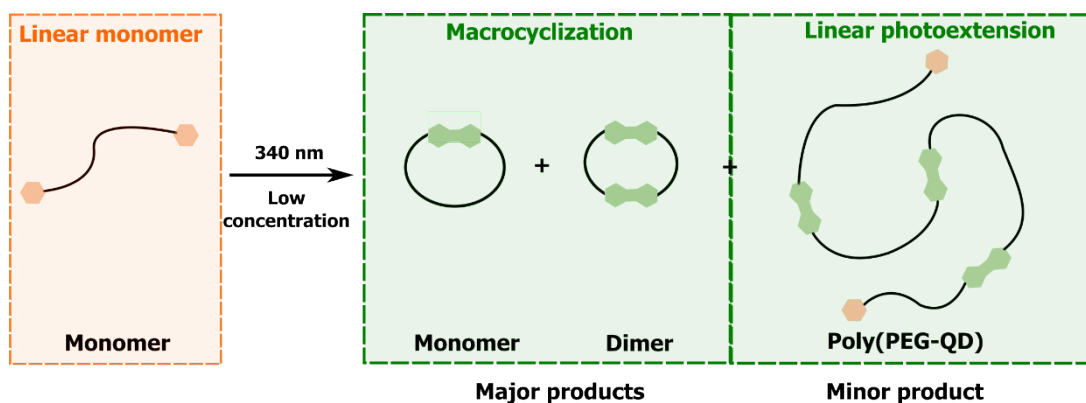


Figure S14. Schematic illustration of the favored intramolecular-driven macrocyclization of linear macromonomers (QM-PEG-QM) and dimers, over the intermolecular-driven linear photoextension, during the photocycloaddition of photoresponsive motifs under dilute conditions.

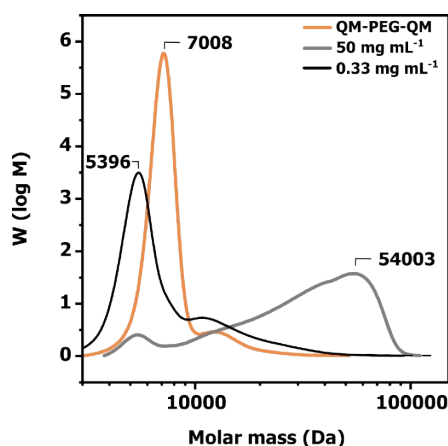


Figure S15. GPC chromatograms QM-PEG-QM (orange), QM-PEG-QM irradiated at 340 nm under oxygen-free conditions at $c = 50 \text{ mg mL}^{-1}$ (grey) and $c = 0.33 \text{ mg mL}^{-1}$ (black) for 25 min and 7 min, respectively. The photoreactions were carried out in ACN solutions, using an LED photoreactor operating at a power of 33 mW.

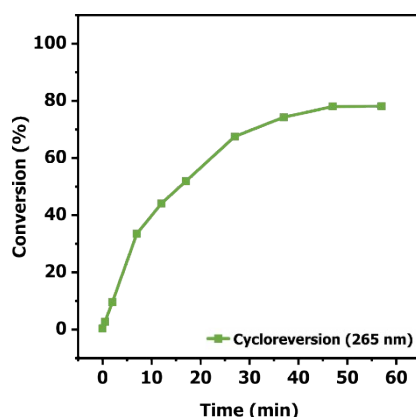


Figure S16. Conversion of poly(PEG-QD) into QM-PEG-QM as function of irradiation time, demonstrating the photodepolymerization of poly(PEG-QD) via cycloreversion at 265 nm under oxygen-free conditions. The photoreaction was carried out at $c = 50 \text{ mg mL}^{-1}$ in an ACN solution, using an LED photoreactor operating at a power of 22 mW.

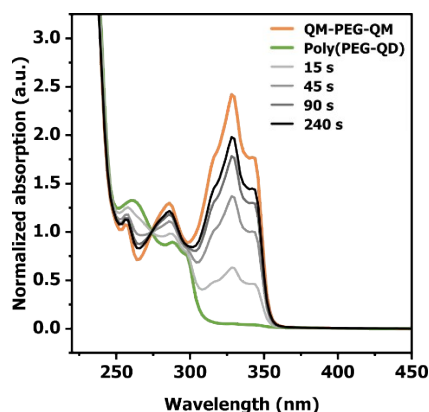


Figure S17. UV-vis absorption spectra of **poly(PEG-QD)** irradiated at 265 nm under oxygen-free conditions at time intervals of 15 to 240 seconds, normalized at 274 nm, illustrating progressive photodepolymerization via cycloreversion. The spectrum of **QM-PEG-QM** (orange) is shown for reference. The photoreaction was carried out in ACN at $c = 1 \text{ mg mL}^{-1}$, using an LED photoreactor operating at a power of 22 mW.

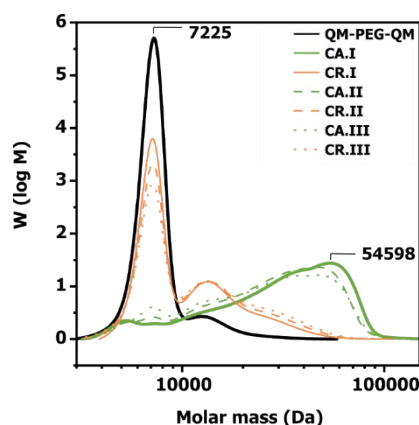


Figure S18. GPC chromatograms of subsequent irradiation cycles of **QM-PEG-QM** (black), sampled after each photocycloaddition, conducted at 340 nm for ca. 25 min (CA, green); and photocycloreversion, conducted at 265 nm for ca. 45 min. (CR, orange). The photoreactions were carried out at $c = 50 \text{ mg mL}^{-1}$ in an ACN solution, using an LED photoreactor operating at power levels ranging from 22 to 33 mW.

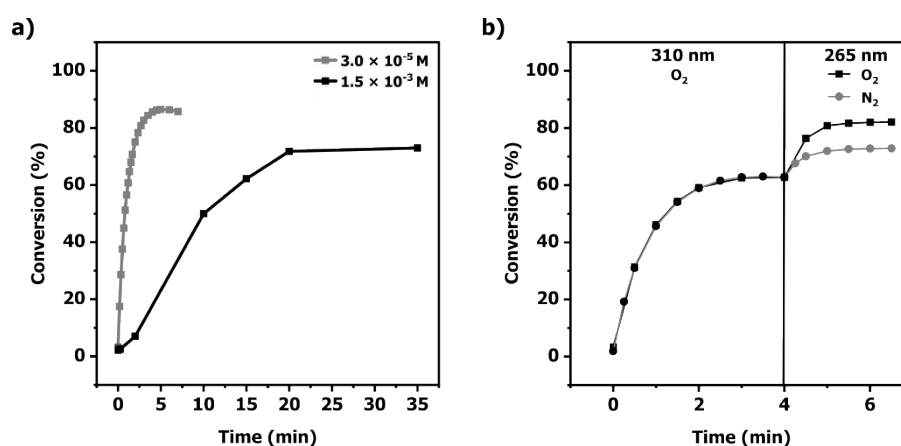


Figure S19. a) Conversions of **QD** into **QM** as function of irradiation time. The cycloreversion was conducted at 310 nm under oxygenated conditions at $c = 3.0 \times 10^{-5} \text{ M}$ (grey) and at $c = 3.0 \times 10^{-5} \text{ M}$ (black). **b)** Conversion of **poly(PEG-QD)** into **QM-PEG-QM** as a function of irradiation time at 310 nm under oxygenated conditions at $c = 0.33 \text{ mg mL}^{-1}$, demonstrating the photodepolymerization via cycloreversion. A second irradiation was subsequently performed at 265 nm, under oxygen-free conditions (grey circles) and oxygenated environment (black squares). Photoreactions were carried out in ACN using an LED photoreactor operating at power levels ranging from 22 to 80 mW.

2 Supporting experimental section

2.1 Materials and instrumentation

2.1.1 Materials

All reagents and solvents were used without further purification, if not specified otherwise. Acetone (puriss.), acetonitrile (ACN) (>99.5%), chloroform (CHCl₃) (>99%), chloroform-*d* (CDCl₃) (99.8%), cyclohexane (>99.5%), dichloromethane (DCM) (>99.5%), N,N-dimethylformamide (DMF) (>99.5%), dimethylsulfoxide-*d*₆ (DMSO-*d*₆) (99.8%), ethyl acetate (EtOAc) (>99%), *n*-hexane (>99%), magnesium sulfate hydrate (MgSO₄) (>99%), methanol (MeOH) (>99%), and silica gel 60 (0.03-0.2 mm) were purchased from Carl Roth. Anhydrous potassium carbonate (K₂CO₃) (99%), 1,6-diisocyanatohexane (99%) (HMDI), iodomethane (MeI) (99%), and Spectra/Por[®] 7 dialysis membrane pre-treated RC tubing (MWCO = 1 kD), were purchased from Thermofisher Scientific. Calcium hydride (CaH₂) (>90%), potassium permanganate (KMnO₄) (puriss.), pyridine hydrochloride (98%), ninhydrin, sodium hydride (NaH) (60% dispersion in paraffin wax) were purchased from Sigma-Aldrich. Dibutyltin-dilaureate (DBTDL) (95%) was purchased from Alfa Aesar. 2,7-dihydroxyquinoline (iminol form of 7-hydroxyquinolin-2(1H)-one) was purchased from BLDpharm. 2-Bromoethanol (>95%) was purchased from TCI. L-Ascorbic acid was purchased from Mivolis. α,ω -Bis-amino poly(ethylene glycol) (PEG-MW 6.000 Da) (H₂N-PEG₆₀₀₀-NH₂) was purchased from abcr. DCM and DMF were dried over MgSO₄ previously pre-heated at 70°C for 24 h, ACN and *n*-hexane were dried over CaH₂; and subsequently distilled. At the exception of ACN which has been used directly, all dried solvents were stored over 4 Å molecular sieves.

2.1.2 Nuclear magnetic resonance (NMR) spectroscopy

NMR Spectroscopy was carried out at 297 K on spectrometers from Bruker: Advance III and Advance II at frequencies of 400 MHz and 250 MHz for ¹H nuclei and 75 MHz for ¹³C nuclei.

Spectra were calibrated to the residual solvent peaks of DMSO-*d*₆ and CDCl₃ at 2.50 ppm and 7.26 ppm, respectively.² Data were treated with MestReNova (14.2) software and all chemical shifts (δ) are reported in parts per million (ppm) with coupling constant in Hz (multiplicity: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, m = multiplet, br = broad signal).

2.1.3 High-performance liquid chromatography (HPLC)

Measurements were conducted using a Shimadzu HPLC LC-40D system, equipped with a Shim-pack GIST C18 column (150 mm length, 4.6 mm internal diameter, and 5 μ m particle size). Each sample was dissolved in a mixture of ACN:water (1:1, v:v), supplemented with 0.1% TFA, to obtain a concentration of ca. 10^{-5} mol L⁻¹.

General Procedure 1: The eluting solvent system consists of water (A) against ACN (B) as the following gradient: 0.0 min: 20% B, 11.0 min: 65% B, 11.5 min: 95% B, 13.5 min: 95% B, 15.0 min: 20% B, 16.0 min 20% B. 10 μ L were injected in the column, the flow rate was set at 1.0 mL min⁻¹. Chromatograms were monitored at 274 nm and the data were acquired directly from the instrument in an ASCII format. *Note:* This method was applied in molecular studies conducted under both oxygen-free and oxygenated conditions.

General Procedure 2: The eluting solvent system consists of water (A) against ACN (B) as the following gradient: 0.0 min: 5% B, 11.0 min: 38% B, 24.5 min: 95% B, 26.5 min: 95% B, 27.0 min: 5% B, 31.0 min: 5% B. 10 to 30 μ L were injected in the column, the flow rate was set at 1.0 mL min⁻¹ and chromatograms were monitored at 274 nm. The data were acquired directly from the instrument in an ASCII format. *Note:* This refined method was developed to improve the identification of side products and achieve better separation of the individual components generated during photochemical reactions under oxygenated conditions.

2.1.4 Ultraviolet-visible light (UV-vis) absorption spectroscopy

Spectra were recorded on a Shimadzu UV-1800 spectrophotometer and data were acquired directly from the instrument in a CSV format. Quartz-cuvettes (1 cm) from Thor Labs were used to measure the absorption from 220 – 450 nm, with 2 nm steps at a slow scan rate.

2.1.5 Fourier-transform infrared (FTIR) spectroscopy

Measurements were carried out on an Agilent Cary 630 FTIR spectrometer equipped with a single bounce diamond ATR sampling accessory. The spectra were recorded in the spectral range of 4000 cm^{-1} to 650 cm^{-1} with a resolution of 4 cm^{-1} for a total of 32 scans to improve the signal-to-noise ratio. The data were acquired from the MicroLab software in CSV format.

2.1.6 Gel Permeations Chromatography (GPC)

GPC experiments were performed on an Agilent 1100 system equipped with one Polymer Standards Service (PSS) styrene-divinylbenzene (SDV) guard column (8 × 50 mm, particle size = 5 μm), two PSS SDV columns (8 × 300 mm, particle size = 5 μm , pore size = 100 Å), and one PSS SDV column (8 × 300 mm, particle size = 5 μm , pore size = 1000 Å). Signals were recorded by a refractive index detector (Agilent 1100 series). Measurements were conducted using THF as the eluent, at 25°C and with a flow rate of 1.0 mL min^{-1} . Molecular weights were determined based on narrow molecular weight polyethylene glycol calibration standards.

2.1.7 GPC coupled with UV-vis detection

GPC experiments were performed on an Agilent 1260 Infinity II system equipped with one PolyPore Guard (ID = 7.5 mm, L = 50 mm) and two Polypore columns (ID = 7.5 mm, L = 300 mm, particle size = 5 μm). Signals were recorded by a refractive index detector

(Agilent 1260 II series) and a multi-angle light scattering detector (Agilent 1260 II series, UV detector, 8 signals, 120 Hz). Measurements were conducted using THF as the eluent, at a temperature of 40°C, and with a flow rate of 1.0 mL min⁻¹. Molecular weights were determined based on narrow molecular weight polystyrene calibration standards.

2.1.8 Photoreactor

Irradiations were carried out with Atlas Photonics Lumos 43 photoreactors equipped with LEDs of various wavelengths (ca. 5 nm half width). The power associated with the utilized LED is indicated in the following table.

Table S1: LED power.

Wavelength (nm)	265	285	310	325	340
Power (mW)	22	60	80	40	33

This instrument is equipped with a power supply, a reactor and sample holders for standard NMR tube, test tube, UV-vis quartz-cuvette (1 cm).

2.2 Methods and procedures

2.2.1 General procedure for preparation of oxygen-free QD stock solutions

QD stock solutions ($c = 3 \times 10^{-5}$ mol L⁻¹) were prepared by dissolving QD in dry ACN in a round-bottom flask. The solutions were subsequently degassed upon three cycles of freeze-pump-thaw, and stored in a glovebox. A small amount of the oxygen-free stock solution (3 mL) was then carefully transferred into a quartz-cuvette. The cuvette was closed using a polytetrafluoroethylene (PTFE) stopper, and sealed with parafilm, before exiting the glovebox.

2.2.2 Photocycloreversion of QD under oxygen-free conditions

The photocycloreversions of **QD** in ACN solutions ($c = 3 \times 10^{-5} \text{ mol L}^{-1}$) were carried out following the general procedure described in **section 2.2.1**. The quartz-cuvettes were placed in the photoreactor using a sample holder. Irradiations were conducted at either 265 nm, 285 nm, 310 nm or 325 nm, and UV-vis spectra were recorded at intervals of 5 to 30 seconds until a plateau was achieved, typically taking 1.5 min to 5 min. It is worth noting that due to the experimental setup, real-time measurements could not be performed, and the irradiation kinetics needed to be momentarily halted for measurement purposes. Furthermore, to mitigate the influence of ongoing irradiation during UV-vis measurement, absorptions were recorded at **QM**'s maximum absorption wavelength, specifically $\lambda = 328 \text{ nm}$. Full spectral measurements were exclusively conducted for the reference spectra (sample at $t = 0 \text{ min}$ before irradiation) and at an early point-time in the conversion plateau, allowing for the subsequent conversion calculations. The conversions c_t at time t were calculated by the following equations 1 and 2:

$$c_t = \frac{A_t}{A_{max}} \cdot 100 \% \quad (1)$$

where A_t is the absorption at time t , and where the absorption at 328 nm for full conversion A_{max} was determined by the following equation 2:

$$A_{max} = \varepsilon_{M, 328} \cdot \left(2 \cdot \left(\frac{A_{0, 288}^*}{\varepsilon_{D, 288}} \right) \right) \quad (2)$$

Where A_0^* is the initial absorption of **QD**, at 288 nm before irradiation ($t = 0 \text{ min}$) and $\varepsilon_{M, 328}$ and $\varepsilon_{D, 288}$ are the extinction coefficients of the monomer at 328 nm and of the dimer at 288 nm, respectively.

Finally, the content of the quartz-cuvettes was submitted to HPLC measurement following the **General Procedure 1** described in **section 2.1.3**.

2.2.3 Photocycloreversion of QD under oxygen atmosphere

The photocycloreversions of **QD** in ACN solutions ($c = 3 \times 10^{-5} \text{ mol L}^{-1}$) were carried out following the general procedure described in **section 2.2.1**. Before irradiation, the quartz-cuvettes were opened and exposed to ambient air for 3 min. The cuvettes were sealed with a PTFE stopper and parafilm, thoroughly shaken and placed in the photoreactor using a sample holder. Irradiations were conducted at either 265, 285, 310 or 325 nm, and UV-vis spectra were recorded at intervals of 5 to 300 seconds until a plateau was achieved, typically taking 2 to 50 min. Conversions c_t were calculated following the equation 1 and 2. Finally, the content of the quartz-cuvettes was submitted to HPLC measurement following the **General Procedure 1** described in **section 2.1.3**.

2.2.4 Wavelength-dependant photon efficiency analysis (WPEA)

Samples for WPEA experiments were prepared according to the abovementioned procedure under nitrogen and oxygen-free conditions. The irradiations were carried out based on the conditions outlined in **table S1**. The photon flux $q_{p,\lambda}$ corresponding to each wavelength λ was estimated by utilizing the output power p_λ of the associated LEDs, with the assumptions of constant output power from the light sources during measurements, and the consideration that all emitted photons enter the reaction mixture. Under these assumptions, the photon flux $q_{p,\lambda}$ is expressed as:

$$q_{p,\lambda} = \frac{p_\lambda \cdot \lambda}{h \cdot c} \quad (3)$$

where h is the Planck constant, and c the speed of light. The reaction time t_λ was then adjusted to reach a fixed number of photons N_p by:

$$t_\lambda = \frac{N_p}{q_{p,\lambda}} \quad (4)$$

The number of photons targeted was fixed at 6.09×10^{19} photons.

2.2.5 Evaluation of the influence of oxygen concentration during the photocycloreversion of QD

An oxygenated **QD** stock solution ($c = 3 \times 10^{-5} \text{ mol L}^{-1}$) was prepared by dissolving **QD** in dry ACN in a round-bottom flask. The mixture was subsequently exposed to ambient air for 1 h. Different volumes (0.00, 0.75, 1.50, 2.25, 3.00 mL) of the stock solution were introduced inside the quartz-cuvettes, which were properly closed and then placed into a glovebox. The cuvettes were subsequently completed to 3 mL by oxygen-free ACN (degassed by freeze-pump-thaw), sealed with a PTFE stopper and parafilm before exiting the glovebox. The quartz-cuvettes were then placed in the photoreactor using a sample holder. Irradiations were conducted at 310 nm and UV-vis spectra were recorded at intervals of 15 to 7200 seconds until a final plateau is reached. Conversions c_t were calculated following the equation 1 and 2.

2.2.6 HPLC monitoring of photocycloreversion of QD at 310 nm under oxygen atmosphere

Quartz-cuvettes were filled with ambient **QD** stock solution (3 mL) described in **section 2.2.5** under oxygen atmosphere. The cuvettes were sealed with a PTFE stopper and parafilm, and placed in the photoreactor using a sample holder. Irradiations were conducted at 310 nm for a given amount of time ranging from 0 to 13 h. Finally, the content of the quartz-cuvettes was submitted to HPLC measurement following **General Procedure 2** described in **section 2.1.3**.

2.2.7 Cyclability test of QD/QM under oxygen atmosphere

A small amount of **QD** stock solution (3 mL) described in **section 2.2.1** was introduced in a quartz-cuvette, and exposed to ambient air for 3 min. The cuvette was sealed with a PTFE

stopper and parafilm, thoroughly shaken and placed in the photoreactor using a sample holder. Execution of cycloreversion and cycloaddition processes was performed at 265 and 340 nm, respectively. Each irradiation step was conducted until reaching the absorption plateau, which occurred in 2 to 15 min for the cycloreversions, and from 173 to 1000 min for the cycloadditions.

Conversions c_t were calculated by the following equation 5.

$$c_t = \left(1 - \frac{A_t}{A_{max}}\right) \cdot 100 \% \quad (5)$$

where A_t is the absorptions of **QM** at time t and A_{max} the maximum absorption of **QM** determined by equation 2. The absorptions of **QM** were measured at 328 nm. An aliquot (ca. 20 μ L) of the solution was sampled after reaching the absorption plateau at each irradiation step, and analysed by HPLC following the **General Procedure 1** described in **section 2.1.3**.

2.2.8 Cyclability test of QD/QM with cycloreversion under oxygen atmosphere and cycloaddition under oxygen-free conditions

A small amount of **QD** stock solution (3 mL) described in **section 2.2.5** was introduced in a quartz-cuvette, sealed with a PTFE stopper and parafilm, and placed in the photoreactor using a sample holder. Execution of cycloreversion and cycloaddition processes was performed at 310 and 340 nm respectively. Each irradiation step was conducted until reaching the absorption plateau, which occurred in 5 min for the cycloreversions, and in 2 min for the cycloadditions.

Before each cycloreversion steps, the solution was oxygenated by bubbling with compressed air for 3 min, and sealed with a PTFE stopper and parafilm. After each cycloreversion steps, oxygen was removed from the solution by bubbling with nitrogen for 30 min, using a syringe (sonicated beforehand for ca. 10 min beforehand in a water bath), and sealed with a PTFE stopper and parafilm. Conversions c_t were calculated following equation 5. An aliquot

(ca. 20 μL) of the solution was sampled after reaching the absorption plateau at each irradiation step, and analysed by HPLC following the **General Procedure 2** described in **section 2.1.3**.

2.2.9 Cyclability test of QM/QD under oxygen-free conditions

A QM solution ($c = 6 \times 10^{-5} \text{ mol L}^{-1}$) was prepared by dissolving QM in dry ACN in a 10 mL Schlenk flask. The solution was subsequently degassed through three cycles of freeze-pump-thaw and stored inside a glovebox. A small amount (3 mL) of the solution was transferred into a quartz-cuvette, sealed with a PTFE stopper and parafilm, and placed in the photoreactor using a sample holder. A sequential execution of cycloaddition and cycloreversion processes was performed at 340 and 265 nm. Each irradiation step was conducted until reaching the absorption plateau, which occurred from 3 to 4 min for the cycloadditions, and from 2 to 3 min for the cycloreversions. The conversions c_t at time t was calculated by the following equation 6:

$$c_t = \left(1 - \frac{A_t}{A_0}\right) \cdot 100 \% \quad (6)$$

where A_t and A_0 are the absorptions of QM at time t and $t = 0 \text{ min}$, respectively. The absorptions of QM were measured at 328 nm.

2.2.10 General procedure for preparation of degassed QM-PEG-QM saturated solutions

QM-PEG-QM saturated solution (50 mg mL^{-1}) was prepared by dissolving 50 mg of QM-PEG-QM in 1 mL of dry ACN, under stirring in a 10 mL Schlenk flask. The solution was subsequently degassed through three cycles of freeze-pump-thaw and placed in a glovebox. The content of the Schlenk was then transferred in a quartz-cuvette, and subsequently sealed with a PTFE stopper and parafilm, before exiting the glovebox.

2.2.11 Cyclability test of QM-PEG-QM/poly(PEG-QD) under oxygen-free conditions

Following the general procedure described in **section 2.2.10**, a QM-PEG-QM saturated solution (50 mg mL^{-1}) was prepared inside a quartz-cuvette, and subsequently placed in the photoreactor using a sample holder. Sequential execution of cycloaddition and cycloreversion processes was performed at 340 and 265 nm, under stirring. The photoprocesses were monitored by UV-vis spectroscopy by sampling aliquots of ca. $20 \mu\text{L}$ at intervals of ca. 2 to 10 min. The aliquots were inserted in a 3 mL quartz-cuvette and completed with ca. 2.98 mL of ACN before measurement. The photoprocesses were monitored until reaching the absorption plateau, occurring from 20 to 25 min for the cycloaddition, and from 40 to 50 min for the cycloreversion. Conversions c_t at time t were calculated following equation 6. After each measurement, the samples were dried under vacuum and analyzed by GPC, following the procedure described in **section 2.1.6**.

2.2.12 Photodepolymerization of poly(PEG-QD) at different concentrations under oxygen atmosphere

Following the general procedure described in **section 2.2.10**, a QM-PEG-QM saturated solution (1 mL, 50 mg mL^{-1}) was prepared inside a quartz-cuvette, which was subsequently placed in the photoreactor using a sample holder. The solution was irradiated at 340 nm until the absorption plateau was reached (ca. 25 min) to form a 1 mL stock solution of **poly(PEG-QD)** ($M_p \approx 60.000 \text{ Da}$, $c = 50 \text{ mg mL}^{-1}$). Aliquots (6.7, 20, and $60 \mu\text{L}$) of the stock solution were introduced in quartz-cuvette, and completed to 3 mL with dry ACN under oxygen atmosphere. Additionally, the stock solution of **poly(PEG-QD)** (ca. 1.0 mL, $c = 50 \text{ mg mL}^{-1}$) was exposed to air for 10 min under stirring. The resulting **poly(PEG-QD)** solutions ($c = 0.11$, 0.33, 1.00, and 50 mg mL^{-1}) were subsequently sealed with a PTFE stopper and parafilm, then placed in the photoreactor using a sample holder. Photocycloreversions were performed at

310 nm under oxygen atmosphere, and monitored by UV-vis spectroscopy until reaching the absorption plateau, occurring from 2 to 20 min. Note that at high concentration ($c = 50.0 \text{ mg mL}^{-1}$), the UV-vis monitoring was only possible by diluting an aliquot (ca. 20 μL) of the solution in 2.98 mL of ACN inside a quartz-cuvette. Conversions c_t at time t were calculated following equations 1 and 2, where A_0^* is the initial absorption of **poly(PEG-QD)**, at 288 nm before irradiation ($t = 0 \text{ min}$). After reaching plateau, the solutions were dried under vacuum and subsequently analyzed by GPC, following the procedure described in **section 2.1.6**.

2.2.13 Follow-up photodepolymerization at 265 nm

Following the general procedure described in **Section 2.2.12**, a partially photodepolymerized solution of **poly(PEG-QD)** ($c = 0.33 \text{ mg mL}^{-1}$) in dry ACN was prepared in a quartz-cuvette by irradiation at 310 nm under an oxygen atmosphere.

Test under oxygen atmosphere

The solution was subsequently submitted to irradiation at 265 nm for ca. 2.5 min.

Test under oxygen-free conditions

The solution was dried under vacuum, introduced in a glovebox and completed to 3 mL with oxygen-free ACN. The quartz-cuvette was then sealed with a PTFE stopper and parafilm, and placed in the photoreactor using a sample holder. The mixture of linear and macrocyclic **QM-PEG-QM** solution was then submitted to irradiation at 265 nm for ca. 2.5 min.

All irradiation experiments were monitored by UV-vis spectroscopy until absorption plateau was reached. Conversions c_t at time t were calculated following equations 1 and 2, where A_0^* is the initial absorption of **poly(PEG-QD)**, at 288 nm before irradiation ($t = 0 \text{ min}$) and $\epsilon_{M, 328}$ and $\epsilon_{D, 288}$ are the extinction coefficients of the monomer at 328 nm and of the dimer at 288 nm, respectively. After each irradiation experiment reached the absorption plateau, the solution was

dried under vacuum and subsequently analyzed by GPC, following the procedure described in **Section 2.1.6**.

2.2.14 Cycloaddition of QM-PEG-QM at $c = 0.33 \text{ mg mL}^{-1}$

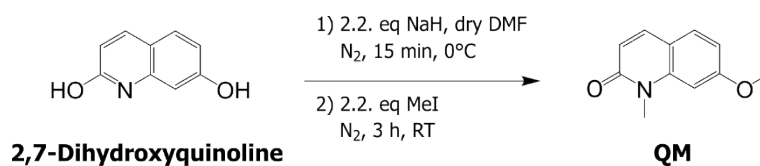
QM-PEG-QM solution (0.33 mg mL^{-1}) was prepared by loading 1 mg of QM-PEG-QM in a 3 mL quartz-cuvette, which was subsequently introduced in a glovebox. The cuvette was then completed with 3 mL of oxygen-free ACN, sealed with a PTFE stopper and parafilm, and placed in the photoreactor using a sample holder. The solution was irradiated at 340 nm until absorption plateau was reached, which occurred at ca. 6 min. Conversions c_t at time t were calculated following equation 5. After reaching plateau, the solution was dried under vacuum and subsequently analyzed by GPC, following the procedure described in **section 2.1.6**.

2.2.15 Dialysis membrane separation

Spectra/Por® 7 dialysis membrane pre-treated RC tubing (MWCO = 1 kD) pieces of 10 to 30 cm were prepared and rinsed in distilled water for 30 min to remove the preservative sodium azide. Polymer reaction mixtures were solubilized in a minimal amount of CHCl_3 :MeOH ((2:1), (v:v)) (ca. 50 mL) and placed inside the dialysis membrane. The membrane was meticulously sealed on both ends with stainless-steel clips, and subsequently placed in a 5 to 10 L bath of CHCl_3 :MeOH ((2:1), (v:v)). The bath was slowly stirred at room temperature, and change every 8 to 16 h, until complete removal of the impurities (ca. 6 days). The presence of impurities in the baths was monitored by TLC using DCM:MeOH ((9:1), (v:v)) as eluent. After proper extraction of the impurities, the content inside the tubing was placed in a round-bottom flask, the solvent was then evaporated under reduced pressure to yield the pure polymer.

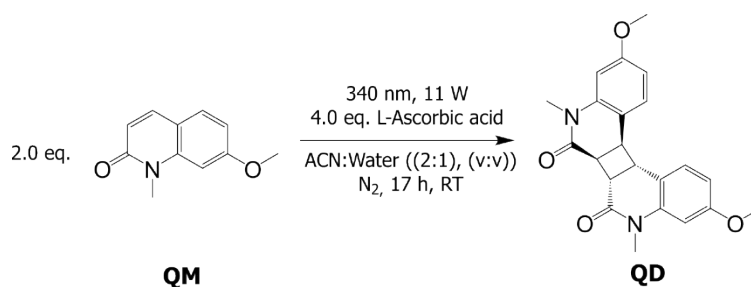
2.3 Synthetic Procedures and Analytical Data

2.3.1 Synthesis of 7-methoxy-1-methylquinolin-2(1H)-one (QM).



7-methoxy-1-methylquinolin-2-one (QM) was synthesized according to previously reported procedures.³ NaH (60% suspension in paraffin wax) (1.64 g, 40.96 mmol, 2.2 eq.) was placed in a two-necked 100 mL pre-dried (heated at ca. 100°C with a heat-gun for 5 min under vacuum) round-bottom flask and purged with nitrogen. The flask was cooled down with an ice-bath (to ca. 0°C) and mixed with dry DMF (30 mL) to produce a mixture containing the compound in suspended form. **2,7-Dihydroxyquinoline** (3.00 g, 18.60 mmol, 1.0 eq.) was slowly added to the suspension and stirred for 15 min at 0°C, followed by a dropwise addition of iodomethane (2.55 mL, 5.81 g, 40.96 mmol, 2.2 eq.). The reaction mixture was warmed up to room temperature and stirred for 3 additional hours. Upon completion of the reaction (monitored by TLC using EtOAc: CyH ((9:1), (v:v)) as eluent), the solution was quenched with water (ca. 20 mL). Then, EtOAc (40 mL) was introduced and the reaction mixture was transferred into a separating funnel. The aqueous phase was partitioned and extracted three times with EtOAc (ca. 40 mL). The organic layers were combined and washed once with water (ca. 100 mL) and three times with brine (ca. 100 mL). The organic phase was then dried over MgSO₄, filtered, and evaporated under reduced pressure. The crude product was purified by flash column chromatography, using EtOAc: CyH ((9:1), (v:v)) as eluent, to afford **QM** (2.15 g, 11.35 mmol, 61%) as a white solid. ¹H-NMR (300 MHz, CDCl₃) δ (ppm): 7.59-7.56 (d, 1H, vinyl -CH), 7.45-7.43 (d, 1H, ArH), 6.82-6.79 (dd, 1H, ArH), 6.77 (m, 1H, ArH), 6.55-6.52 (d, 1H, vinyl -CH), 3.91 (s, 3H, -OCH₃), 3.67 (s, 3H, -NCH₃). ¹³C-NMR (75.4 MHz, CDCl₃) δ (ppm): 162.89, 161.93, 141.87, 138.85, 130.23, 118.67, 115.05, 109.72, 98.80, 55.73, 29.59.

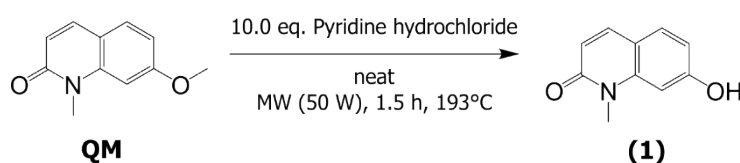
2.3.2 Synthesis of anti-head-to-head quinolinone dimer (QD)



QM (1 g, 5.3 mmol, 2.0 eq.) was dissolved in acetonitrile (17 mL) inside a Schlenk tube and the solution was stirred under nitrogen atmosphere for 30 min. The mixture was heated to ca. 80°C to achieve proper dissolution. After a suitable dissolution, the mixture was allowed to cool down to room temperature. L-Ascorbic acid (1.83 g, 10.6 mmol, 4.0 eq.) was added in the mixture and was dissolved with addition of water (ca. 8 mL) upon stirring. The solution was then irradiated at 340 nm for 17 h with LEDs (55 mW). The solution was cool down in an ice bath to effectively precipitate the desired **QD**. The white solid was filtrated, washed with water (20 mL) and dried under vacuum, to afford **QD** (226.0 mg, 0.60 mmol, 22.6%) as a white solid. ¹H-NMR (300 MHz, CDCl₃) δ (ppm): 6.84-6.82 (d, 2H, ArH), 6.59 (d, 2H, ArH), 6.54-6.51 (dd, 2H, ArH), 3.82 (s, 6H, -OCH₃), 3.71-3.70 (m, 4H, cyclobutane-CH), 3.43 (s, 6H, -NCH₃). ¹³C-NMR (75 MHz, CDCl₃) δ (ppm): 169.45, 159.88, 140.87, 128.55, 116.12, 106.87, 102.88, 55.57, 43.92, 43.54, 29.83.

Note: Despite the observation of an impurity at 1.89 ppm in the spectra, suspected to be water, this compound was used without further purification.

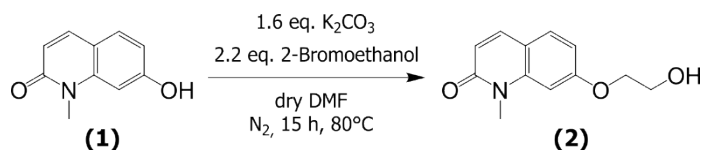
2.3.3 Synthesis of 7-hydroxy-1-methylquinolin-2-one (**1**)



QM (1.0 g, 5.28 mmol, 1.0 eq.) and pyridine hydrochloride (6.1 g, 52.8 mmol, 10.0 eq.) were combined and thoroughly mixed in a beaker until obtention of a homogeneous solid, which was

subsequently placed in a 35 mL microwave vial. The reaction was performed under microwave irradiation at 193°C with a power of 50 W under high stirring for 1.5 h. The resulting brown solid was then poured into iced water (100 mL) under stirring to form a white suspension which was then isolated by filtration and washed with additional water (50 mL). The resulting solid was dried under high vacuum and purified by flash column chromatography, using EtOAc as eluent to afford **(1)** (415.9 mg, 2.38 mmol, 45%) as a white powder. ¹H-NMR (300 MHz, DMSO-*d*₆) δ (ppm): 10.25 (s, 1H, -OH), 7.76-7.73 (d, 1H, vinyl -CH-), 7.53-7.50 (d, 1H, ArH), 6.80-6.70 (m, 2H, ArH), 6.36-6.33 (d, 1H, vinyl -CH-), 3.52 (s, 3H, -NCH₃). ¹³C-NMR (75.4 MHz, DMSO-*d*₆) δ (ppm): 161.49, 160.16, 141.69, 139.11, 130.31, 116.62, 113.17, 111.08, 100.00, 28.86.

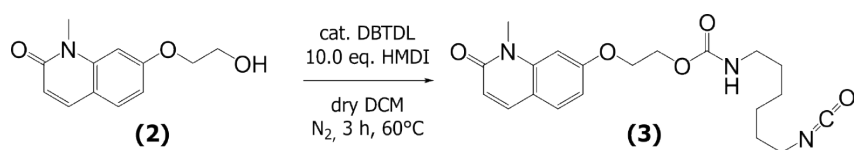
2.3.4 Synthesis of 7-(2-hydroxyethoxy)-1-methylquinolin-2-one (**2**)



Compound **(1)** (276.0 mg, 1.58 mmol, 1.0 eq.) and K₂CO₃ (350.0 mg, 2.53 mmol, 1.6 eq.) were placed in a 25 mL pre-dried Schlenk flask (heated at ca. 100°C with a heat-gun for 5 min under vacuum), and dissolved in dry DMF (8 mL), under nitrogen atmosphere. The reaction mixture was heated at 80°C and stirred for 15 min until proper dissolution of the chemicals. 2-Bromoethanol (440.7 mg, 0.25 mL, 3.53 mmol, 2.2 eq.) was added dropwise and the mixture further stirred at 80°C for 15 h. The reaction was monitored by TLC using EtOAc as eluent. Upon completion of the reaction, the solvent was fully evaporated under reduced pressure. The residue was adsorbed on silica gel and purified by flash column chromatography. The elution of the unreacted starting material **(1)** was realized with EtOAc, until its full collection (monitored by TLC in EtOAc), then the same column was eluted with EtOAc:MeOH ((97:3), (v:v)) to afford the functionalized product **(2)** (226.6 mg, 1.03 mmol,

66%) as a pale orange solid. $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ (ppm): 7.82-7.79 (d, 1H, vinyl-*CH*), 7.64-7.61 (d, 1H, *ArH*), 6.94-6.88 (m, 2H, *ArH*), 6.43-6.40 (d, 1H, vinyl-*CH*), 4.95-4.91 (t, 1H, -*OH*), 4.16-4.13 (t, 2H, O- $\text{CH}_2\text{CH}_2\text{OH}$), 3.79-3.74 (m, 2H, O- $\text{CH}_2\text{CH}_2\text{OH}$), 3.59 (s, 3H, - NCH_3). $^{13}\text{C-NMR}$ (75.4 MHz, $\text{DMSO-}d_6$) δ (ppm): 161.43, 160.95, 141.45, 138.93, 130.14, 117.59, 114.12, 110.17, 99.31, 70.00, 59.50, 29.01.

2.3.5 Synthesis of (3)

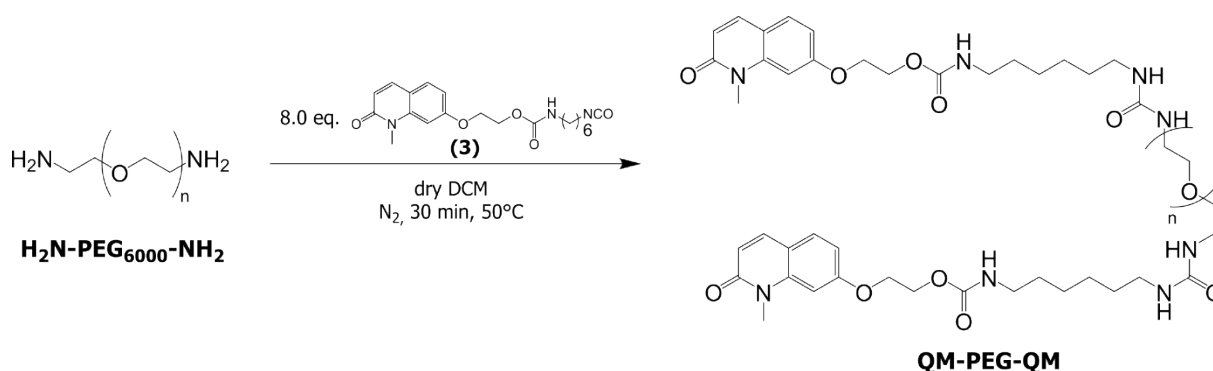


Compound (2) (600.0 mg, 2.74 mmol, 1.0 eq.) was placed in a 100 mL pre-dried round-bottom flask (heated at ca. 100°C with a heat-gun for 5 min under vacuum), under nitrogen atmosphere, dried for 30 min at room temperature under vacuum and dissolved in 50 mL of dry DCM. The solution was heated at 60°C until complete dissolution of the component. HMDI (4.40 mL, 27.4 mmol, 10.0 eq.) was quickly injected in the reaction mixture. In parallel, a drop of DBTDL was diluted in 2 mL of dry DCM in a separate flask and 0.5 mL of this solution was subsequently added to the reaction mixture. The system was stirred under nitrogen atmosphere and reflux at 60°C for 3 h. The reaction was then allowed to cool down to room temperature and the solvent was reduced to ca. 5-10 mL under vacuum. The resulting mixture was then precipitated in cold dry *n*-hexane (ca. 40 mL) and further washed eight times with cold dry *n*-hexane (ca. 20 mL), to afford (3) (741.5 mg, 1.91 mmol, 70%) as a white solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.60-7.58 (d, 1H, vinyl-*CH*), 7.47-7.45 (d, 1H, *ArH*), 6.83 (m, 2H, *ArH*), 6.57-6.55 (d, 1H, vinyl-*CH*), 4.82 (br, 1H, *NH*), 4.47 (s, 2H, $\text{CH}_2\text{-O(CO)}$), 4.27 (s, 2H, ArO-CH_2), 3.67 (s, 3H, - NCH_3), 3.29 (t, 2H, $\text{CH}_2\text{-NCO}$), 3.22-3.14 (m, 2H, $\text{CH}_2\text{-NH(CO)}$), 1.60-1.37 (m, 8H, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$ from hexyl-carbamate). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3)

δ (ppm): 162.84, 160.87, 156.30, 141.85, 138.78, 130.28, 118.98, 115.35, 109.85, 99.75, 67.00, 63.03, 42.99, 41.09, 31.25, 29.97, 29.62, 26.34, 26.22.

Note: The ^{13}C -NMR spectrum shows no distinct signal for the carbon of the isocyanate ($-\text{NCO}$) group, likely due to signal broadening caused by rapid relaxation. Nevertheless, a weak resonance at 122.50 ppm—typical for NCO carbons—was detected in the HMBC spectrum, displaying a long-range C–H correlation with the ^1H signal at 3.29 ppm ($\text{CH}_2\text{--NCO}$).^{4–6} The FTIR spectrum further confirms the presence of the isocyanate functionality through a characteristic stretching band at 2271 cm^{-1} (see **Supporting Molecular Characterization**).⁷

2.3.6 Synthesis of QM-PEG-QM



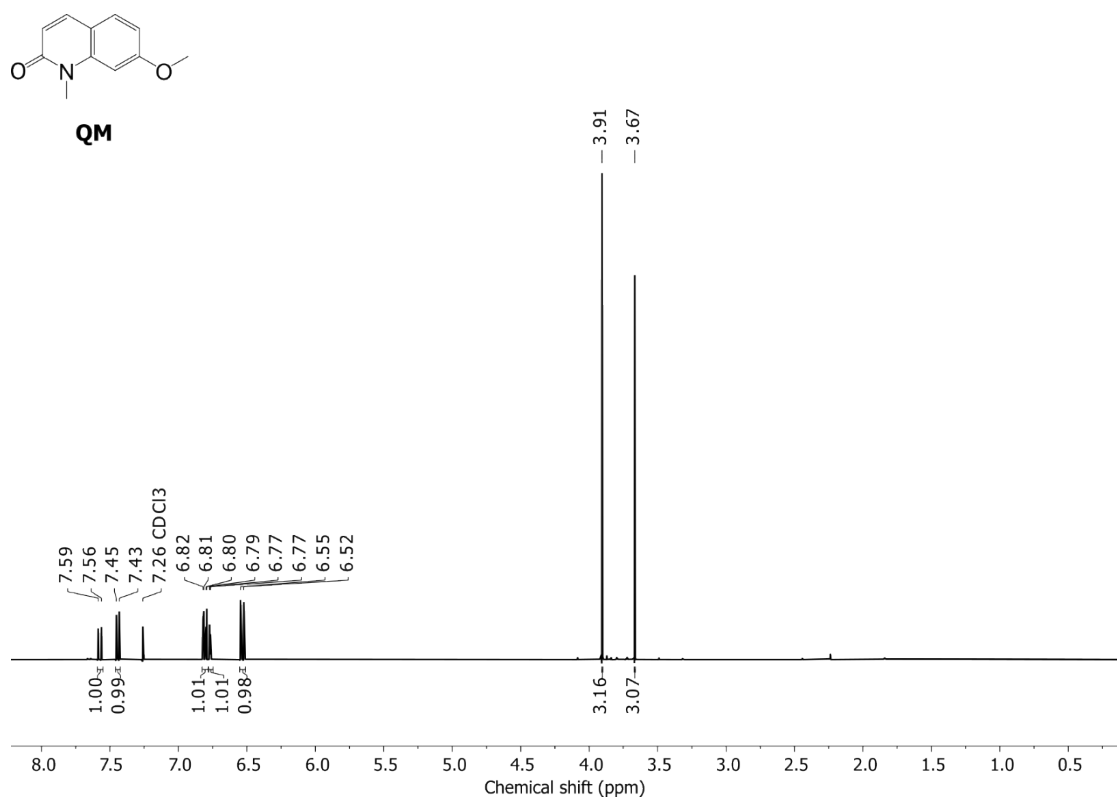
$\text{H}_2\text{N-PEG}_{6000}\text{-NH}_2$ (900.3 mg, 0.15 mmol, 1.0 eq.), was stirred and dried under vacuum at 80°C for 24 h in a round-bottom flask (500 mL). The system was allowed to cool down at room temperature, compound **(3)** (500.0 mg, 1.2 mmol, 8.0 eq.) was introduced and the mixture was stirred under vacuum for 1 h. Then, dry DCM (130 mL) was added under nitrogen until full dissolution of the components. The reaction was stirred at 50°C for 30 min under nitrogen. The reaction was monitored by ^1H -NMR spectroscopy by tracking the disappearance of the triplet signal at 2.86 ppm corresponding to the CH_2 in alpha of the amine of $\text{H}_2\text{N-PEG}_{6000}\text{-NH}_2$ (see **Supporting Molecular Characterization**). After completion of the reaction, the crude product was subjected to the dialysis procedure, detailed in **section 2.2.15** to yield **QM-PEG-QM** (947.1 mg, 0.14 mmol, 93%) as a white solid.

H₂N-PEG₆₀₀₀-NH₂: ¹H-NMR (250 MHz, CDCl₃) δ (ppm): 3.92-3.36 (dt, O-¹³CH₂-CH₂-O), 3.64 (m, 392H, PEG-*H*), 3.51(t, 2H, PEG-OCH₂-CH₂-NH), 2.86 (t, 2H, PEG-OCH₂-CH₂-NH₂). GPC (THF, versus PEG standard) M_n: 5621 g mol⁻¹, M_w: 5867 g mol⁻¹, Đ: 1.044.

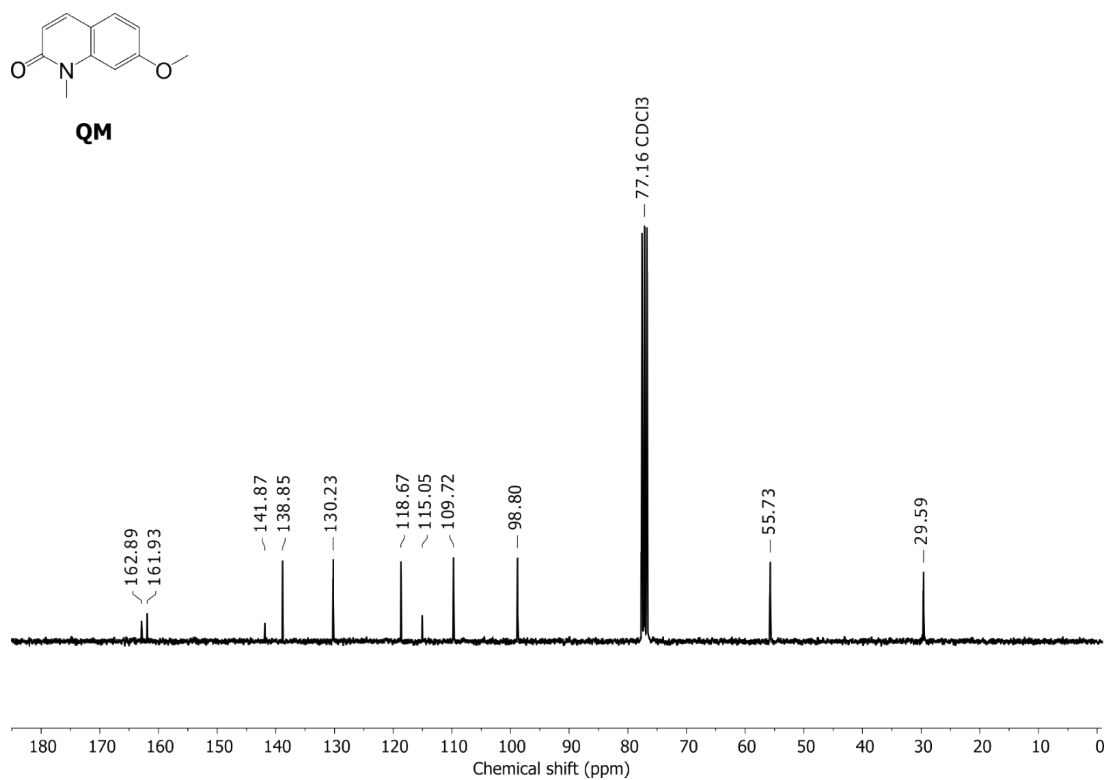
QM-PEG-QM: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.61-7.59 (d, 1H, vinyl-*CH*-), 7.48-7.46 (d, 1H, Ar*H*), 6.84-6.82 (m, 2H, Ar*H*), 6.57-6.54 (d, 1H, vinyl-*CH*-), 5.00 (br, 1H, NH), 4.44 (t, 2H, CH₂-O(CO)), 4.27 (t, 2H, ArO-CH₂O), 3.81-3.45 (dt, O-¹³CH₂-CH₂-O), 3.67 (s, 3H, N-CH₃), 3.64 (m, 395H, PEG-*H*), 3.53 (t, 2H, PEG-OCH₂-CH₂-NH), 3.35 (t, 2H, PEG-OCH₂-CH₂-NH), 3.20-3.12 (m, 4H, CH₂-CH₂-NH(CO)), 1.47 (m, 4H, N(H)-CH₂-CH₂-CH₂), 1.32-1.24 (m, 4H, CH₂-CH₂-CH₂-CH₂). GPC (THF, versus PEG standard) M_n: 7079 g mol⁻¹, M_w: 7694 g mol⁻¹, Đ: 1.087.

2.4 Supporting Molecular Characterization

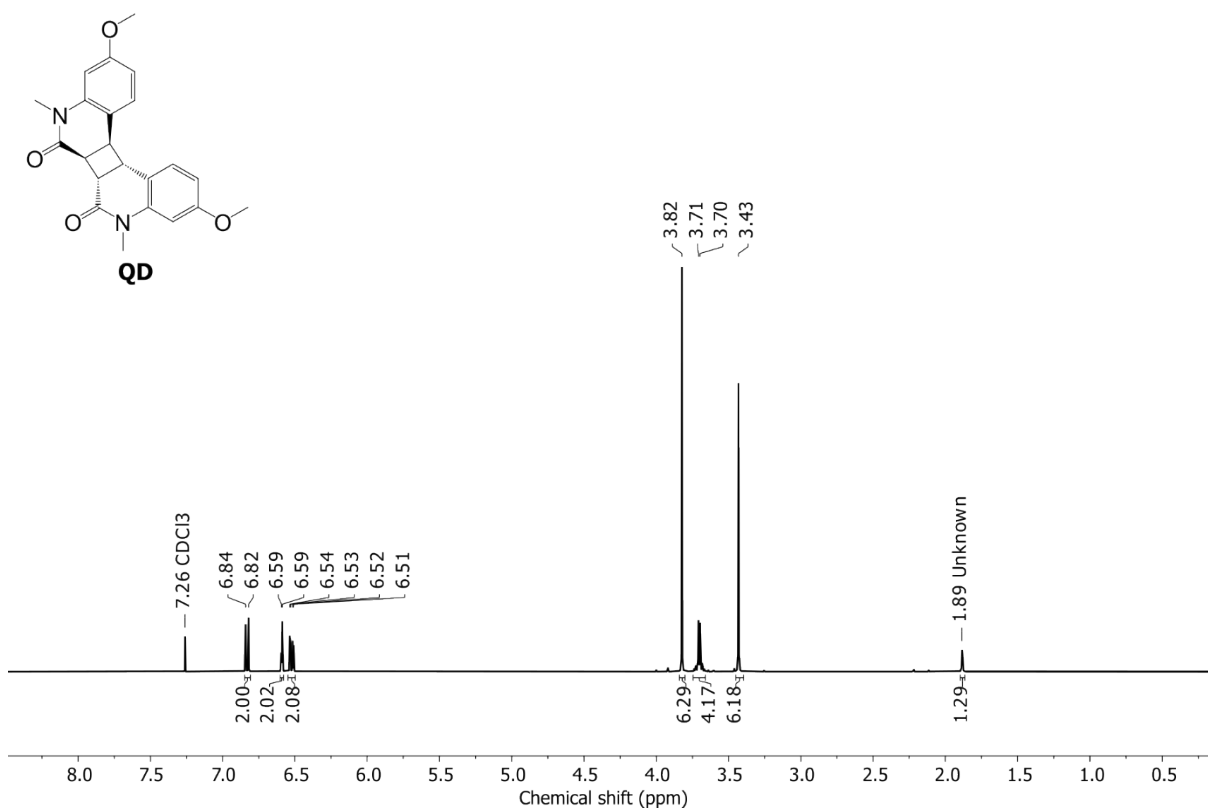
$^1\text{H-NMR}$ spectrum of **QM** in CDCl_3 .



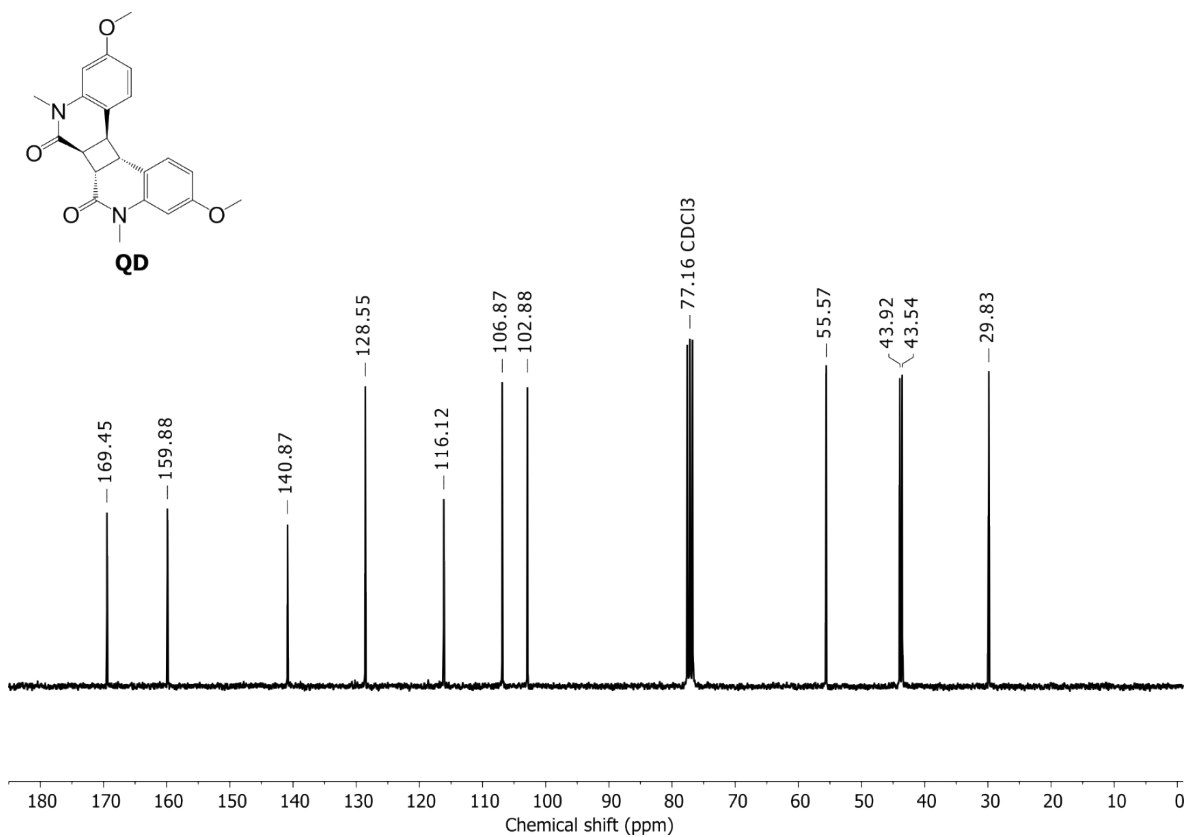
$^{13}\text{C-NMR}$ spectrum of **QM** in CDCl_3 .



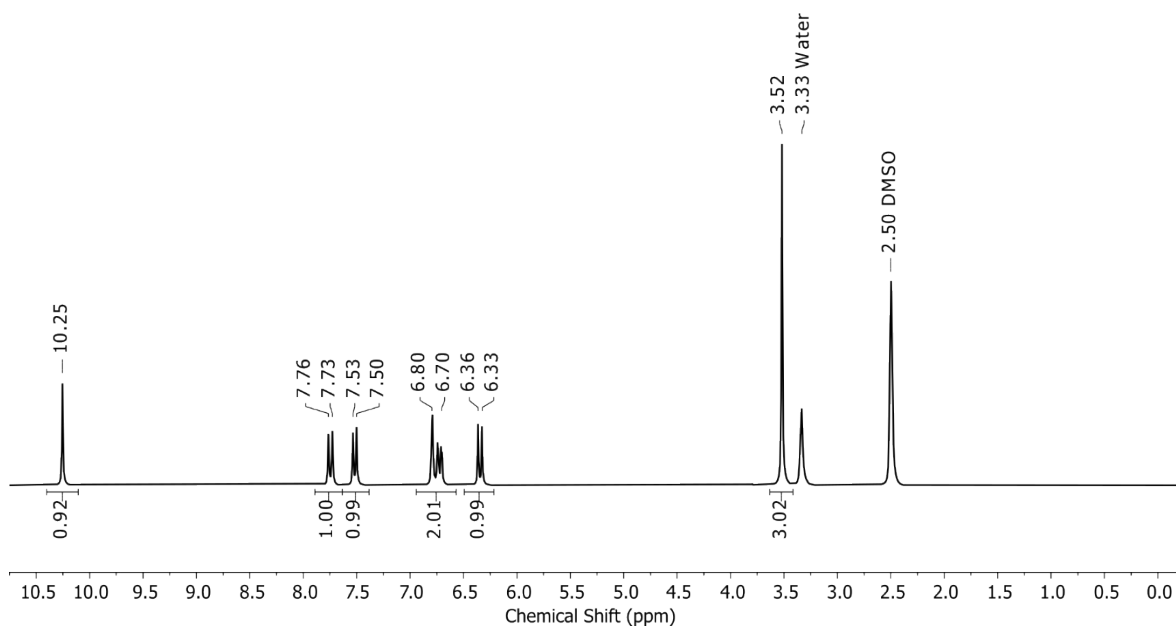
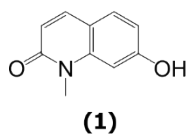
$^1\text{H-NMR}$ spectrum of **QD**_{aHH} in CDCl_3 .



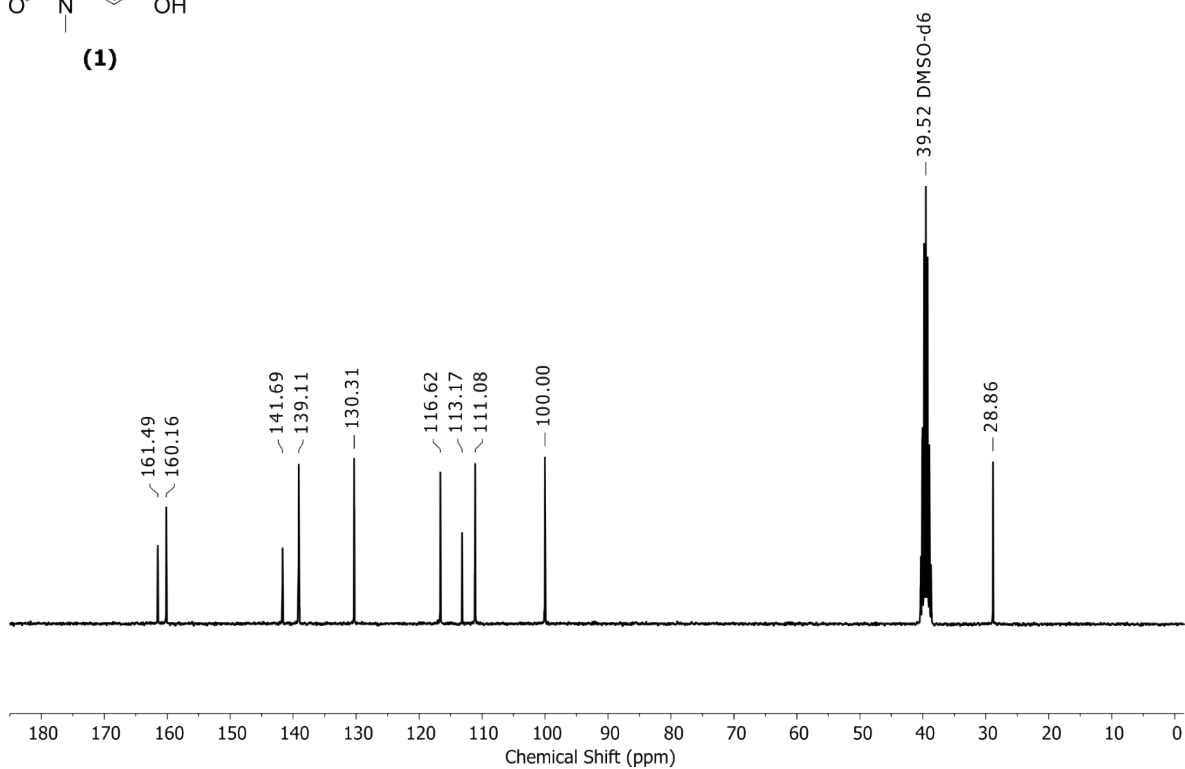
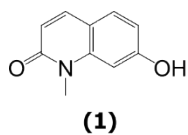
$^{13}\text{C-NMR}$ spectrum of **QD** in CDCl_3 .



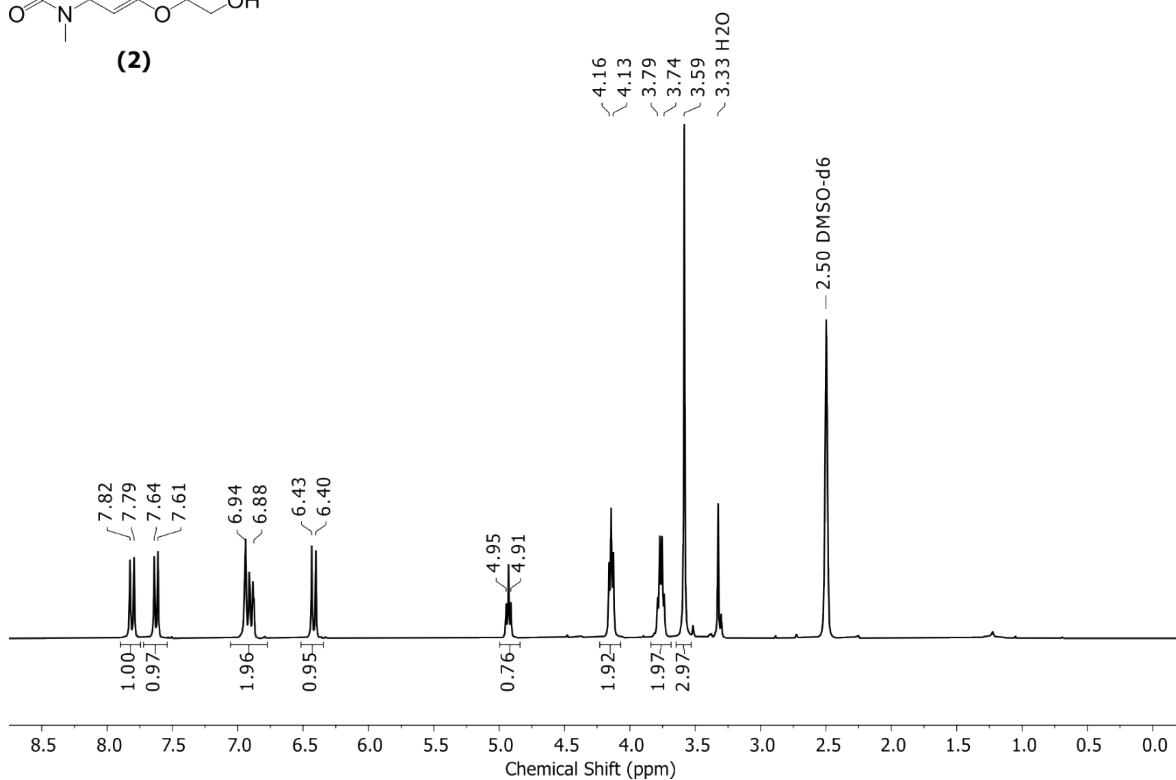
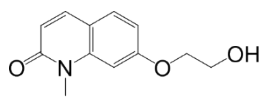
$^1\text{H-NMR}$ spectrum of **(1)** in DMSO-d_6 .



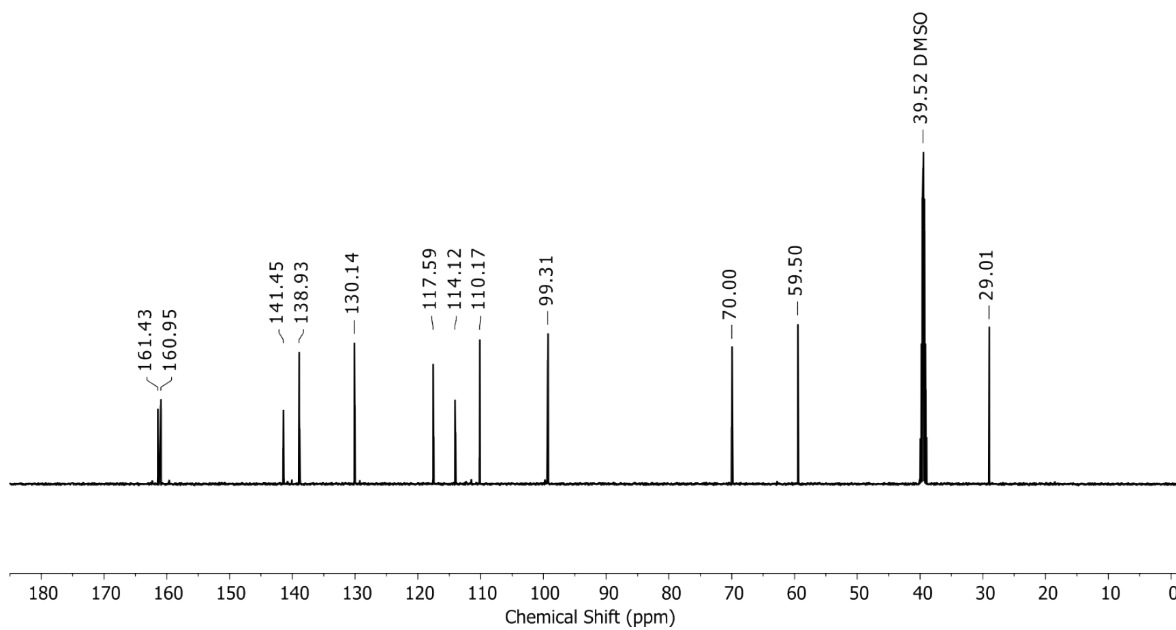
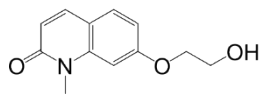
$^{13}\text{C-NMR}$ spectrum of **(1)** in DMSO-d_6 .



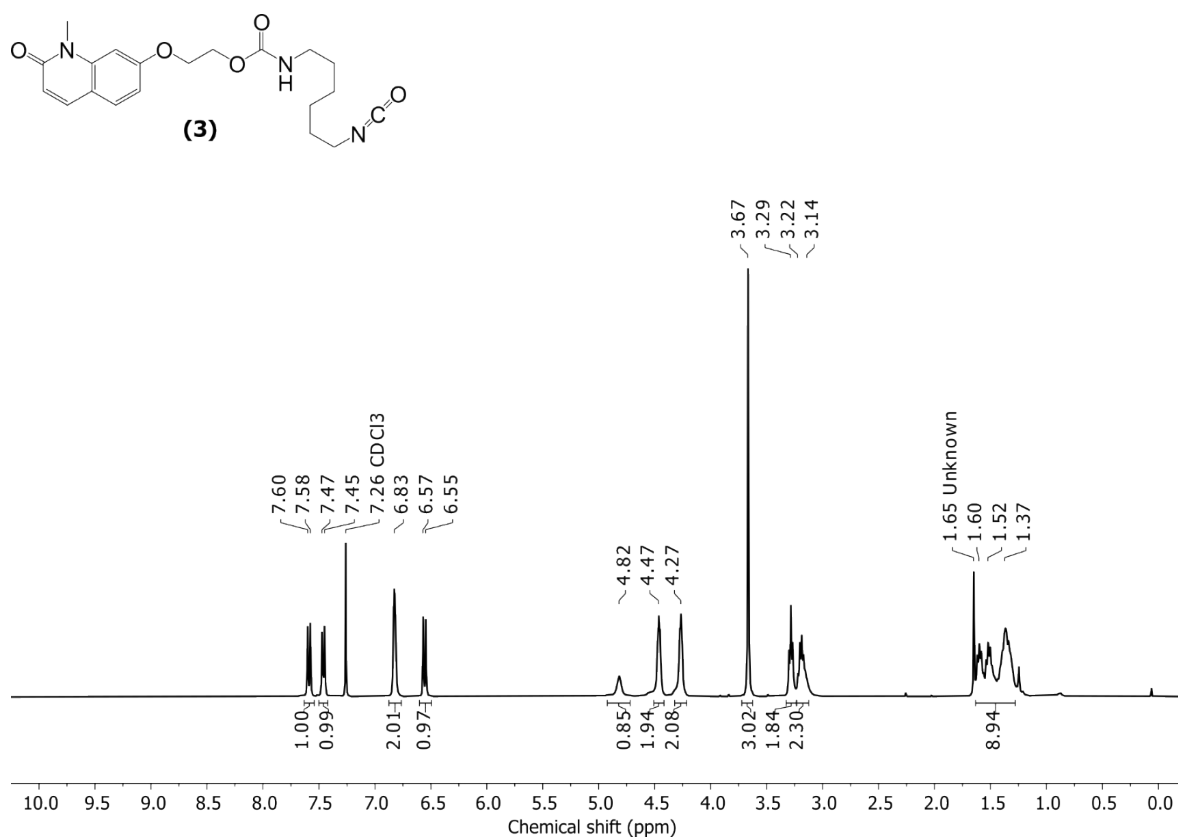
¹H-NMR spectrum of (2) in DMSO-d₆.



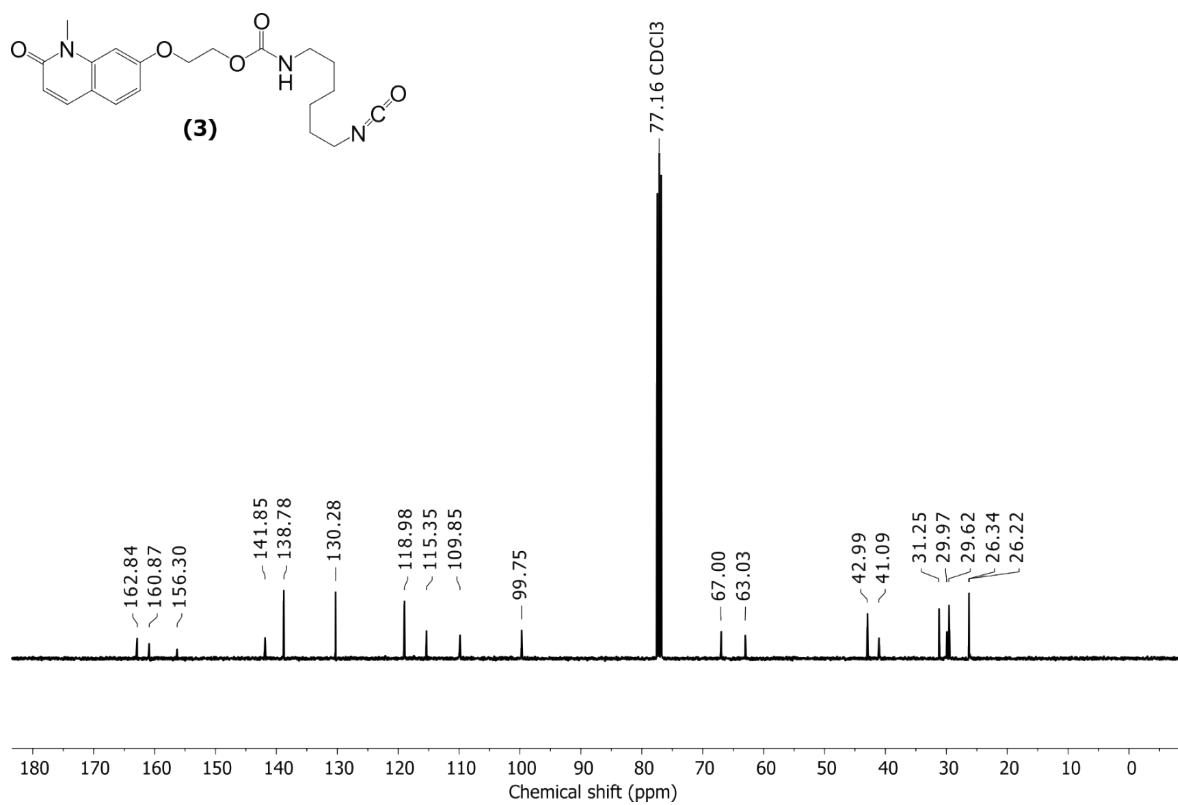
¹³C-NMR spectrum of (2) in DMSO-d₆.



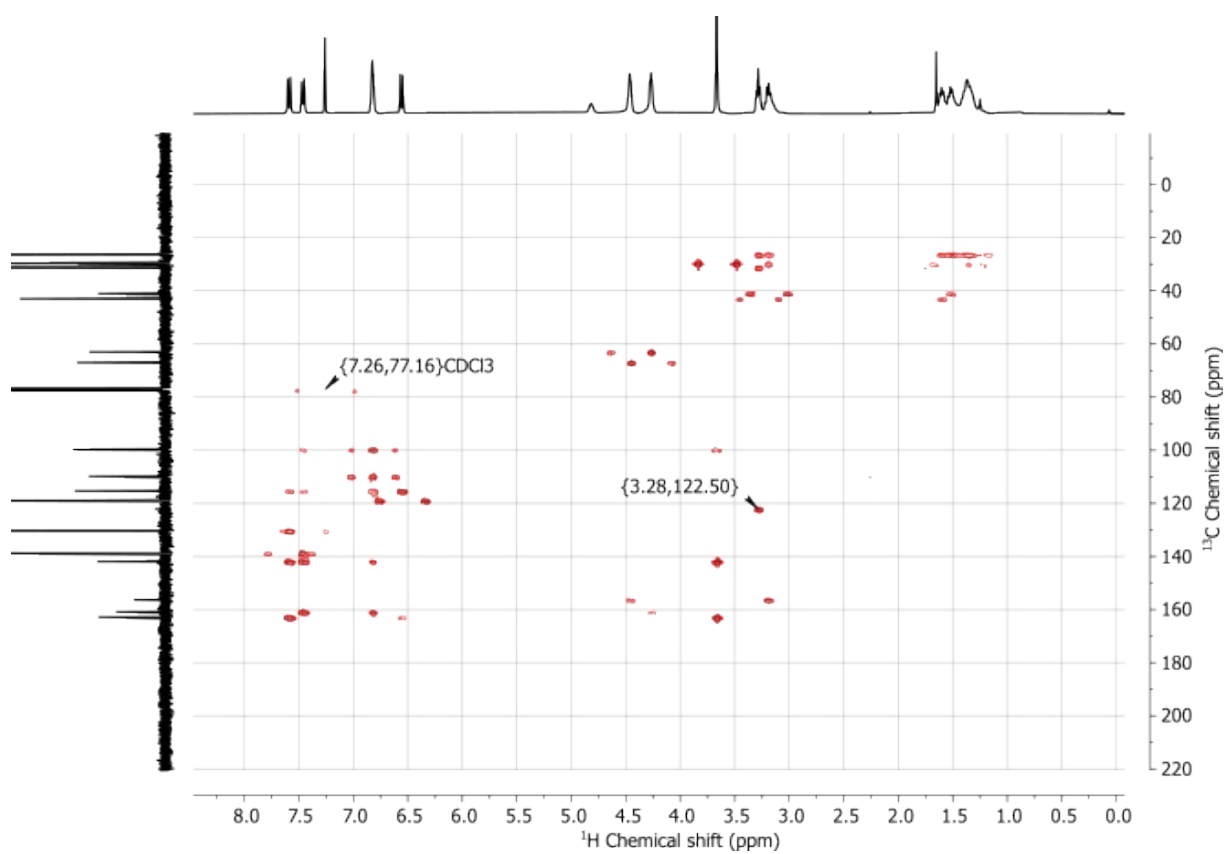
$^1\text{H-NMR}$ spectrum of **(3)** in CDCl_3 .



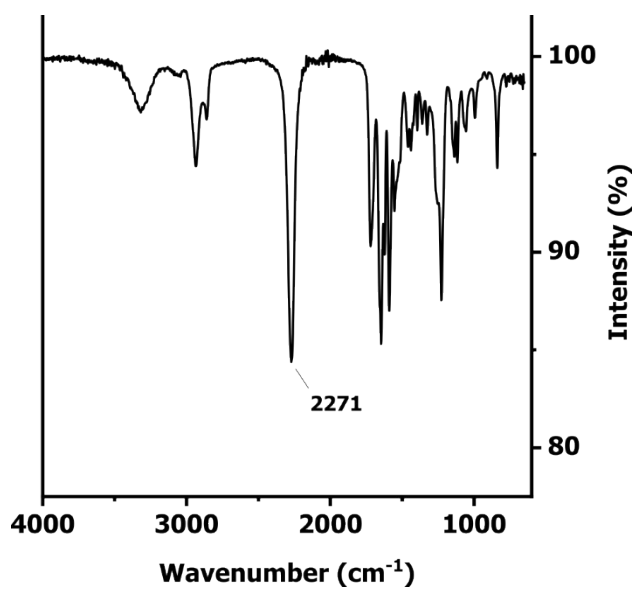
$^{13}\text{C-NMR}$ spectrum of **(3)** in CDCl_3 .



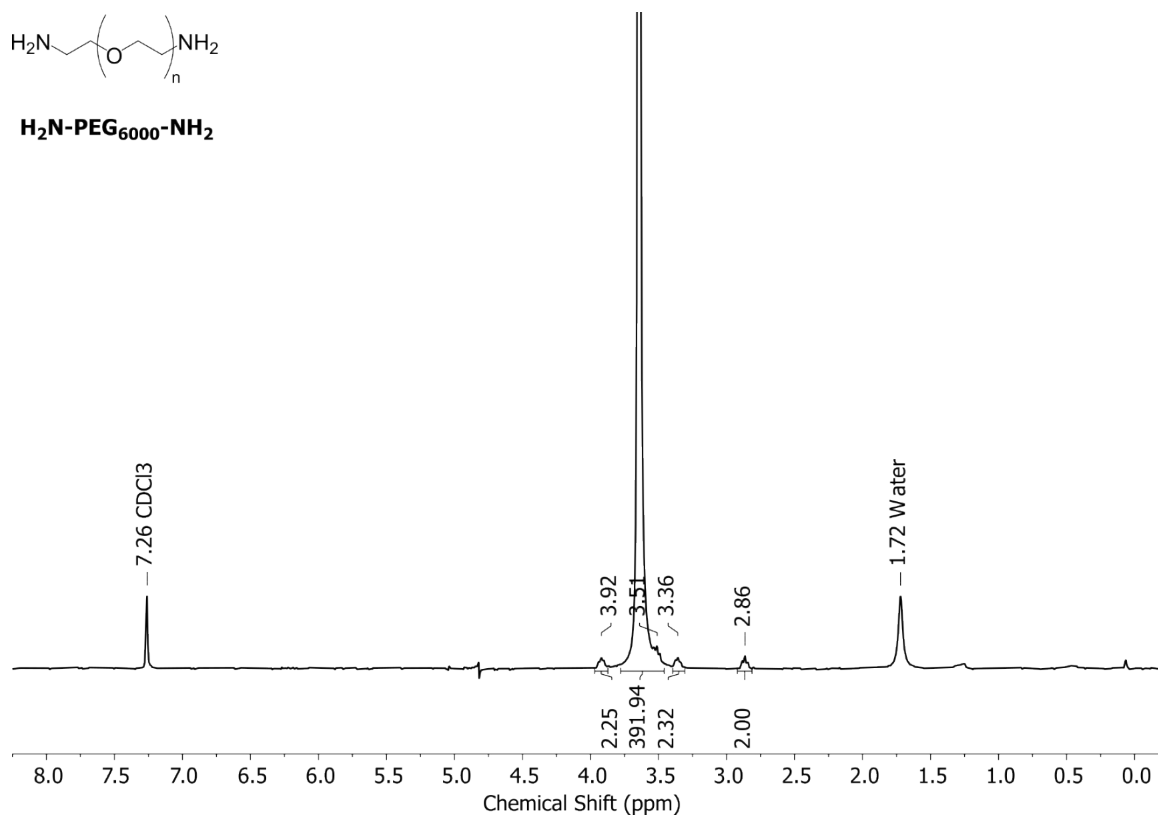
HMBC 2D spectrum of **(3)** in CDCl₃.



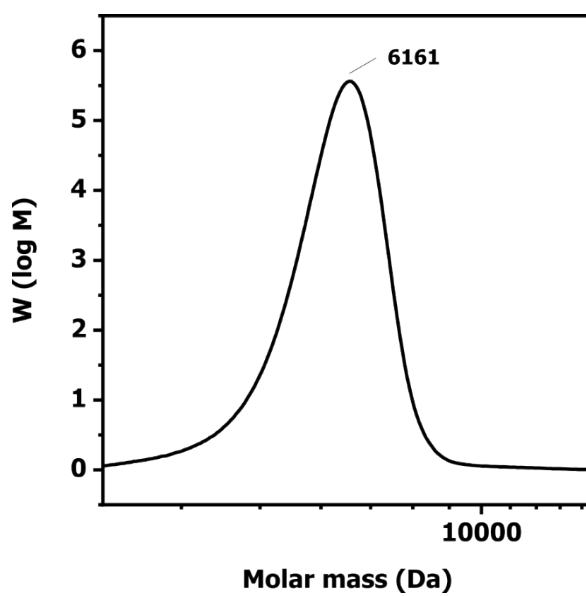
FTIR spectrum of **(3)**.



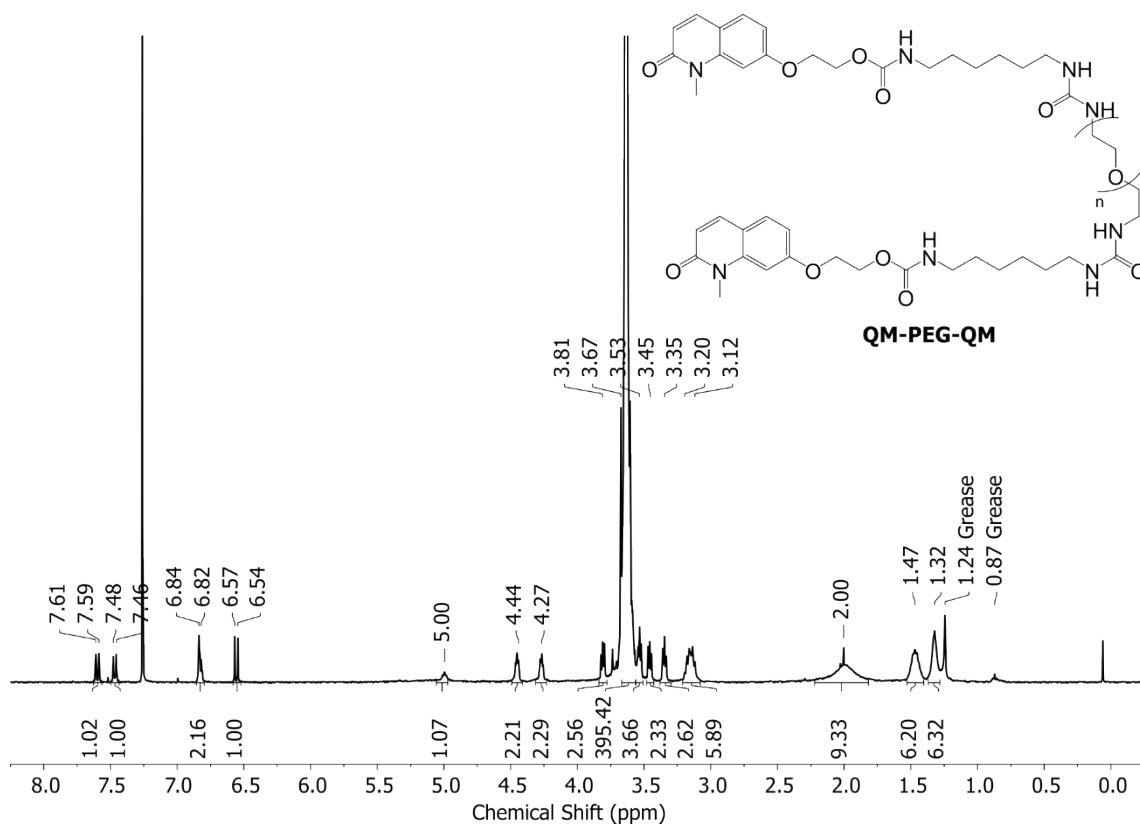
$^1\text{H-NMR}$ spectrum of $\text{H}_2\text{N-PEG}_{6000}\text{-NH}_2$ in CDCl_3 .



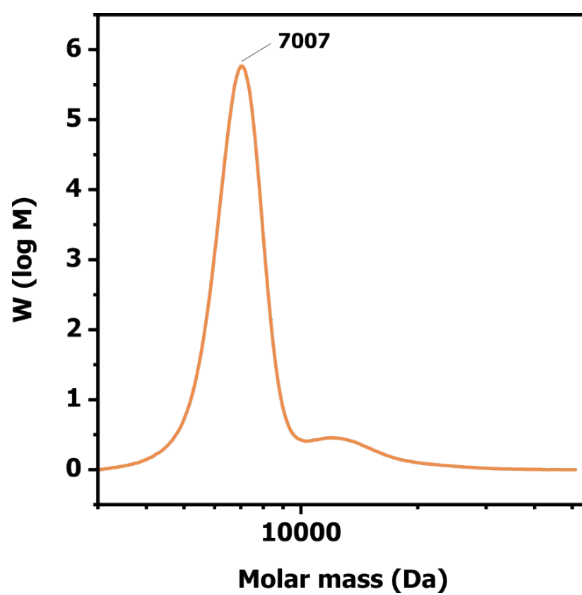
GPC chromatogram of $\text{H}_2\text{N-PEG}_{6000}\text{-NH}_2$.



$^1\text{H-NMR}$ spectrum of QM-PEG-QM in CDCl_3 .



GPC chromatogram of QM-PEG-QM.



3 References

- 1 N. Bieniek, C. P. Haas, U. Tallarek and N. Hampp, *Photochemical & Photobiological Sciences*, 2021, **20**, 773–780.
- 2 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
- 3 N. Paul, M. Jiang, N. Bieniek, J. L. P. Lustres, Y. Li, N. Wollscheid, T. Buckup, A. Dreuw, N. Hampp and M. Motzkus, *J Phys Chem A*, 2018, **122**, 7587–7597.
- 4 R. Glaser, R. Hillebrand, W. Wycoff, C. Camasta and K. S. Gates, *J Org Chem*, 2015, **80**, 4360–4369.
- 5 K. Hatada, K. Ute, K.-I. Oka and S. P. Pappas, *J Polym Sci A Polym Chem*, 1990, **28**, 3019–3027.
- 6 H. J. Reich, Organic Chemistry Data: NMR Spectroscopy, https://organicchemistrydata.org/hansreich/resources/nmr/?index=nmr_index%2F13C_shift#pdata177, (accessed 26 August 2025).
- 7 A. Nandiyanto, R. Ragadhita, M. Fiandini and I. Ijost, *Indonesian Journal of Science and Technology*, 2023, **8**, 113–126.