Complex Molecular Logic Gates from Simple Molecules

Osvaldo J. Quintana-Romero, Armando Ariza-Castolo
Departamento de Química, Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, Av. IPN 2508, San Pedro Zacatenco, 07360, Ciudad de México.

Content:

| General information | S3 |
|---------------------|----|
| Synthesis: methodology 1–3 | S3 |
| Spectra conditions | S3 |
| Operation cycle determination methodology information | S4 |
| Molecular logic gates | S4-S23 |
| 5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (6) | S4 |
| 1H NMR spectra of compound 6 | S5 |
| (E)-6-((1H-pyrrol-2-yl)methylene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (7): | S6 |
| 1H and 13C NMR spectra of compound 7 | S7-S8 |
| (E)-6-(4-methoxybenzylidene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (8) | S9 |
| 1H and 13C NMR spectra of compound 8 | S10-S11 |
| (E)-6-(2-hydroxybenzylidene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (9) | S12 |
| 1H and 13C NMR spectra of compound 9 | S13-S14 |
| (E)-6-((1,1'-biphenyl)-4-yl)methylene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (10) | S15 |
| 1H and 13C NMR spectra of compound 10 | S16-S17 |
| (E)-6-(anthracen-9-ylmethylene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (11) | S18 |
| 1H and 13C NMR spectra of compound 11 | S19-S20 |
| (E)-6-((E)-3-phenylallylidene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (12) | S21 |
| 1H and 13C NMR spectra of compound 12 | S22-S23 |
| Absorption spectrums UV/Vis of MLG after irradiation light. | S24-S26 |
| Titration procedure | S26 |
| Table S1. Calculated protonation constants K | S26 |
| Figure S12. Titration of MLG 7 with pTSOH | S27 |
| Figure S13. Titration of MLG 8 with pTSOH | S28 |
| Figure S14. Titration of MLG 9 with pTSOH | S29 |
| Figure S15. Titration of MLG 10 with pTSOH | S30 |
| Figure S16. Titration of MLG 11 with pTSOH | S31 |
| Figure S17. Titration of MLG 12 with pTSOH | S32 |
| Figure S18–S21. NMR nOe-dpfgse spectra of MLG E-11 | S33-S36 |
| Experimental determination of MLG operation | S37 |
|--------------------------------------------|-----|
| Figure S22. Image of photoirradiation experiment. | S37 |
| Figure S23. $^1$H NMR spectrums of compounds $E-7$, $Z-7$, and $E-7H^*$. | S38 |
| Figure S24. $^1$H NMR spectrums of compounds $E-8$, $Z-8$, and $E-8H^*$. | S39 |
| Figure S25. $^1$H NMR spectrums of compounds $E-9$, $Z-9$, and $E-9H^*$. | S40 |
| Figure S26. $^1$H NMR spectrums of compounds $E-10$, $Z-10$, and $E-10H^*$. | S41 |
| Figure S27. $^1$H NMR spectrums of compounds $E-11$, $Z-11$, and $E-11H^*$. | S42 |
| MLG operation process | S43-S48 |
| Figure S28. Scheme of MLG 7 operation process | S43 |
| Figure S29. Scheme of MLG 8 operation process. | S44 |
| Figure S30. Scheme of MLG 9 operation process. | S45 |
| Figure S31. Scheme of MLG 10 operation process. | S46 |
| Figure S32. Scheme of MLG 11 operation process. | S47-S48 |
| Chart S1. Proposed molecule of $E-12$ decomposition by 400 nm light. | S48 |
| Figure S33. Scheme of MLG 12 operation process. | S49 |
| Description of Operation Process for MLG 8, 9, and 10. | S50-S55 |
| Scheme S1. Operation cycle of MLG 8. | S50 |
| Scheme S2. Operation cycle of MLG 9. | S52 |
| Scheme S3. Operation cycle of MLG 10. | S54 |
| Table S2. Summary of results for each process performed to verify MLGs 7 and 11. | S56 |
| Figure S34. Scheme of MLG 7 and 11 operating in the same NMR tube. | S57 |
| Table S3. Summary of method of operation for the mixture of MLGs 7 and 11, outputs and corresponding labels | S58 |
| Scheme S4. Diagrams of the logical operation solved with the mixture of MLGs 7 and 11 with the theoretical labels | S59-S60 |
| Table S4. Summary of results of each process performed to verify for the mixture of MLGs 7, 10 and 11. | S61 |
| Figure S35. Operating process for MLG 7, 10 and 11 | S62 |
| Table S5. Digitalization responses of the process and the logical operation solved for the mixture of MLGs 7, 10 and 11 | S63 |
| Scheme S5. Diagrams for the logical operation solved with the mixture of MLGs 7, 10 and 11 with the theoretical labels | S64-S68 |
| Theory calculation of MLG $E-7$ | S68-70 |
| Figure S36. Structure of MLG E-7 refined with DFT. | S69 |
| Table S5. Comparation data of DFT methods for $E-7$ simulate UV/Vis absorption spectra | S69 |
| Figure S37. Theory UV/Vis absorption spectra of $E-7$. | S70 |
| Figure S38. Orbitals of transitions states of $E-7$ | S71 |
**General information**

All reagents were purchased from Sigma-Aldrich and used without previous purification. The NMR spectra were recorded using a JEOL ECA-500 spectrometer with a magnetic field of 11.75 T (1H, 500.160 MHz; 13C, 125.765 MHz). The unified scale was used with TMS as reference diluted (volume fraction \( \varphi < 1\% \)) in chloroform for \(^1\text{H}\) resonance ((CH\(_3\))\(_4\)Si \( ^1\text{H}, ^{13}\text{C} = 0 \)). The UV/Vis absorption spectra were recorded with a Perkin Elmer Lambda 2S UV-VIS spectrophotometer. Low resolution mass spectra were acquired with HPLC/coupled mass Agilent Technologies (ESI).

**Synthesis**

*Methodology 1*

In a round-bottom flask, 1.12 mmol of potassium hydroxide were dissolved in 12 mL of methanol under stirring and a solution of ketone 6 (0.37 mmol in 3 mL of methanol) was added dropwise followed by dropwise addition of a solution of 2-pyrrole carboxaldehyde (0.48 mmol in 3 mL of methanol). The reaction mixture was maintained under vigorous stirring for 3 days at room temperature. After the reaction time, the organic phase was extracted with methylene chloride/200 mL of brine solution and concentrated under vacuum. The product was purified by chromatographic column using mixtures of Hexane:Ethyl Acetate of increasing polarity as eluent.

*Methodology 2*

2-Pyrrrole carboxaldehyde (0.48 mmol), ketone 6 (0.37 mmol) and 0.75 mmol of sodium sulphate were placed in a 15 mL vial followed by dropwise addition of 0.2 mL of piperidine and the reaction mixture was maintained under vigorous stirring agitation for 1 day at room temperature. After the reaction time, the organic phase was extracted with methylene chloride/1% hydrochloric acid aqueous solution, evaporated under vacuum and the product was purified by column chromatography using Hexane:Ethyl acetate mixtures of increasing polarity as eluent.

*Methodology 3*

To a 10 mL vial, 0.37 mmol of 2-pyrrole carboxaldehyde, 0.37 mmol of Ketone 6 and 0.4 mL of ethanol were added, the reaction mixture was left under stirring until a homogeneous solution was formed. Subsequently, the reaction mixture was placed in an ice bath and a 5% aqueous solution of potassium hydroxide was added dropwise until formation of a precipitate. Then 5 mL of water were added and the reaction mixture was allowed to freeze. The frozen solution was allowed to reach room temperature and filtered under vacuum.

**Spectra conditions**

The NMR spectra were recorded at 21.1°C using a Jeol ECA-500 at \( B_0 = 11.75 \) T (\(^1\text{H}\) at 500.159 MHz and \(^{13}\text{C}\) at 125.76 MHz). All spectra were recorded in CDCl\(_3\) solution in 5 mm OD tubes. The compounds were assigned using the pfg-COSY, pfg-HMBC and pfg-HSQC pulse sequences. The UV-Vis spectra were determined using a Perkin Elmer Lambda 2S spectrometer; to obtain the coefficient absorptions we did a standard curve (Concentration/Absorption) with 3 concentrations (3X10\(^{-5}\)M, 5X10\(^{-5}\)M, 7X10\(^{-5}\)M) and then
we could calculate the absorption epsilon with slope. The Mass spectra were recorded with ESI-API.

**Operation cycle determination methodology information**

In a 5 mm OD NMR tube, a solution of the corresponding MLG in the concentration indicated was prepared. The NMR tube was irradiated with an Aldrich® Micro Photochemical Reactor. The NMR tube was placed close to the LEDs using an aluminum tube to maintain a firm vertical position. Blue irradiation with a wavelength of 445 nm and violet irradiation with a wavelength of 400 nm were used. All $^1$H NMR spectra were recorded at 500 MHz.

**Molecular logic gates**

![Molecular logic gates diagram]

**5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (6):**

$^1$H NMR (CDCl$_3$, 500 MHz): H$_2$ δ 8.77 (1H, d, $J = 3.8$ Hz), H$_4$ δ 7.90 (1H, d, $J = 7.4$ Hz), H$_3$ δ 7.45 (1H, dd, $J = 4.5$, 10.0 Hz), H$_6$ δ 3.17 (2H, m, $J = 6.3$ Hz), H$_5$ δ 2.77 (2H, m).
(E)-6-((1H-pyrrol-2-yl)methylene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (7):

$^1$H NMR (DMSO d6, 500 MHz): H10 δ 11.62 (1H, s), H2 δ 8.68 (1H, dd, $J$ = 1.4, 4.5 Hz), H4 δ 8.06 (1H, dd, $J$ = 1.4, 7.7 Hz), H3 δ 7.54 (1H, dd, $J$ = 4.5, 7.7 Hz), H15 δ 7.53 (1H, s), H11 δ 7.17 (1H, hex, $J$ = 1.4 Hz), H13 δ 6.74 (1H, s), H12 δ 6.32 (1H, m), H5 δ 3.94 (2H, s).

$^{13}$C ($^1$H) NMR (CDCl3, 125 MHz): δ C7 192.03, C9 156.06, C2 150.54, C6 144.71, C4 135.58, C14 129.03, C3 127.60, C8 127.46, C15 125.31, C11 124.89, C13 115.50, C12 112.29, C5 30.40.

ES-API $m/z$: M+ 211.0.

Absorption coefficient in CHCl3: 21000 cm⁻¹

**Figure S1.** Absorption UV/Vis spectrum of **E-7** in CHCl3 (with DMSO drops) at room temperature with concentration of 5X10⁻⁵ M.
(E)-6-(4-methoxybenzylidene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (8):

$^1$H NMR (DMSO d6, 500 MHz): H2 δ 8.68 (1H, dd, J = 1.4, 4.5 Hz), H4 δ 8.14 (1H, dd, J = 1.4, 7.7 Hz), H13 δ 7.71 (2H, d, J = 8.8 Hz), H15 δ 7.66 (1H, s), H3 δ 7.61 (1H, dd, J = 4.5, 8.1 Hz), H12 δ 7.03 (2H, d, J = 8.8 Hz), H5 δ 4.06 (2H, s), H10 δ 3.84 (3H, s).

$^{13}$C ($^1$H) NMR (CDCl3, 125 MHz): C7 δ 193.74, C11 162.39, C9 154.77, C2 150.05, C6 145.48, C15 136.00, C4 135.80, C13 133.28, C14 130.80, C3 127.87, C8 127.46, C12 114.39, C10 54.87, C5 29.85.

ES-API m/z: M⁺ 252.2.

Absorption coefficient in CHCl₃: 28000 cm⁻¹

**Figure S2.** Absorption UV/Vis spectrum of E-8 in CHCl₃ at room temperature with concentration of 5X10⁻⁵ M.
(E)-6-(2-hydroxybenzylidene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (9):

$^1$H NMR (CD$_3$OD, 500 MHz): H$_2$ δ 8.65 (1H, dd, $J = 1.4, 4.5$ Hz), H$_{17}$ δ 8.52 (1H, s), H$_4$ δ 8.10 (1H, dd, $J = 1.4, 7.7$ Hz), H$_{13}$ δ 7.61 (1H, dd, $J = 1.4, 8.1$ Hz), H$_3$ δ 7.55 (1H, dd, $J = 4.5, 7.7$ Hz), H$_{15}$ δ 7.10 (1H, td, $J = 2.1, 8.4$ Hz), H$_{16}$ δ 6.70 (1H, dd, $J = 1.0, 8.4$ Hz), H$_{14}$ δ 6.51 (1H, t, $J = 7.4$ Hz), H$_5$ δ 3.32 (2H, s). $^1$

$^3$C ($^1$H) NMR (CDCl$_3$, 125 MHz): δ C$_7$ 193.17, C$_{11}$ 170.13, C$_9$ 155.49, C$_1$ 149.43, C$_6$ 144.95, C$_{17}$ 135.84, C$_4$ 135.51, C$_{15}$ 132.68, C$_{13}$ 129.78, C$_8$ 127.52, C$_2$ 127.15, C$_{12}$ 123.63, C$_{16}$ 120.69, C$_{14}$ 114.29, C$_5$ 29.93.

ES-API m/z: M$^+$ 238.3.

Absorption coefficient in CHCl$_3$: 10000 cm$^{-1}$

**Figure S3.** Absorption UV/Vis spectrum of E-9 in CHCl$_3$ (with DMSO drops) at room temperature with concentration of 5X10$^{-5}$ M.
**PLM E-10**

(E)-6-[(1,1'-biphenyl)-4-ylmethylene]-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (10):

$^1$H NMR (CDCl$_3$, 500 MHz): H2 $\delta$ 8.83 (1H, d, $J = 3.8$ Hz), H4 $\delta$ 8.00 (1H, d, $J = 7.7$ Hz), H18 $\delta$ 7.86 (1H, s), H16 $\delta$ 7.76 (2H, d, $J = 8.1$ Hz), H15 $\delta$ 7.70 (2H, d, $J = 8.1$ Hz), H12 $\delta$ 7.63 (2H, d, $J = 7.7$ Hz), H3 $\delta$ 7.51 (1H, dd, $J = 4.5$, 7.7 Hz), H11 $\delta$ 7.47 (2H, t, $J = 7.7$ Hz), H10 $\delta$ 7.40 (1H, d, $J = 1.2$ Hz), H5 $\delta$ 4.12 (2H, s).

$^{13}$C ($^1$H) NMR (CDCl$_3$, 125 MHz): $\delta$ C7 192.70, C9 155.03, C2 150.76, C6 144.37, C13 143.08, C14 140.00, C18 136.00, C4 135.14, C17 133.90, C8 132.35, C16 131.63, C11 129.08, C10 128.18, C15 127.79, C3 127.56, C12 127.20, C5 30.71.

ES-API m/z: M⁺ 298.3.

Absorption coefficient in CHCl$_3$: 27000 cm$^{-1}$

**Figure S4.** Absorption UV/Vis spectrum of **E-10** in CHCl$_3$ at room temperature with concentration of 5X10$^{-5}$ M.
PLM E-10

X: parts per Million: 13C
(E)-6-(anthracen-9-ylmethylene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (11):

$^1$H NMR (CDCl$_3$, 500 MHz): H$_2$ $\delta$ 8.78 (1H, d, $J = 4.2$ Hz), H$_{18}$ $\delta$ 8.69 (1H, s), H$_{17}$ $\delta$ 8.46 (1H, s), H$_{12}$, H$_{15}$ $\delta$ 8.01 (4H, m), H$_4$ $\delta$ 7.63 (1H, d, $J = 7.7$ Hz), H$_{13}$, H$_{14}$ $\delta$ 7.47 (4H, m), H$_3$ $\delta$ 7.36 (1H, dd, $J = 4.5, 7.7$ Hz), H$_5$ $\delta$ 3.35 (2H, s).

$^{13}$C ($^1$H) NMR (CDCl$_3$, 125 MHz): $\delta$ C$_7$ 191.91, C$_9$ 155.39, C$_2$ 150.95, C$_8$ 144.88, C$_6$ 139.32, C$_{18}$ 134.92, C$_4$ 134.52, C$_{17}$ 131.33, C$_{10}$ 129.19, C$_{12}$ 129.14, C$_{11}$ 129.05, C$_3$ 128.24, C$_{16}$ 127.69, C$_{13}$ 126.57, C$_{14}$ 125.60, C$_{15}$ 125.50, C$_5$ 29.46.

ES-API $m/z$: M$^+$ 322.4.

Absorption coefficient in CHCl$_3$: 1400 cm$^{-1}$

Figure S5. Absorption UV/Vis spectrum of E-11 in CHCl$_3$ at room temperature with concentration of 5X10$^{-5}$ M.
(E)-6-((E)-3-phenylallylidene)-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (12):

$^1$H NMR (CDCl$_3$, 500 MHz): H2 $\delta$ 8.77 (1H, d, $J$ = 4.4 Hz), H4 $\delta$ 7.91 (1H, d, $J$ = 7.7 Hz), H14, H11 $\delta$ 7.52 (3H, m), H3 $\delta$ 7.43 (1H, dd, $J$ = 4.7, 6.4 Hz), H12 $\delta$ 7.36 (2H, td, $J$ = 1.2, 7.8 Hz) H13 $\delta$ 7.33 (2H, td, $J$ = 1.2, 7.0 Hz), H16, H15 $\delta$ 7.06 (2H, m), H5 $\delta$ 3.86 (2H, s).

$^{13}$C ($^1$H) NMR (CDCl$_3$, 125 MHz): $\delta$ C7 192.40, C9 156.32, C2 150.70, C8 143.72, C16 143.36, C6 136.14, C14 135.64, C4 134.91, C10 133.73, C13 129.69, C12 129.07, C11 127.58, C3 127.31, C15 123.70, C5 28.47.

ES-API m/z: M+ 248.2.

Absorption coefficient in CHCl$_3$: 17000 cm$^{-1}$

Figure S6. Absorption UV/Vis spectrum of **E-12** in CHCl$_3$ at room temperature with concentration of 5X10$^{-5}$ M.
**Irradiation response UV/vis spectrum**

![Graph](image1)

**Figure S7.** Absorption UV/Vis spectrum of *E*-7 after irradiation with light of 400 nm for 7 min, in CHCl₃ at room temperature with concentration of 5X10⁻⁵ M. (Possible *Z*-7 absorption spectrum)

![Graph](image2)

**Figure S8.** Absorption UV/Vis spectrum of *E*-8 after irradiation with light of 400 nm for 7 min, in CHCl₃ at room temperature with concentration of 5X10⁻⁵ M. (Possible *Z*-8 absorption spectrum)
**Figure S9.** Absorption UV/Vis spectrum of $E-9$ after irradiation with light of 400 nm for 7 min, in CHCl$_3$ at room temperature with concentration of 5X10$^{-5}$ M. (Possible $Z-9$ absorption spectrum)

**Figure S10.** Absorption UV/Vis spectrum of $E-10$ after irradiation with light of 400 nm for 7 min, in CHCl$_3$ at room temperature with concentration of 5X10$^{-5}$ M. (Possible $Z-10$ absorption spectrum)
Figure S11. Absorption UV/Vis spectrum of E-11 after irradiation with light of 445 nm for 7 min, in CHCl₃ at room temperature with concentration of 3X10⁻⁵ M. (Possible Z-11 absorption spectrum)

We did not print the spectrum of E-12 after de irradiation because we did not observe any signal in the spectrum. Therefore, the irradiation of E-12 was studied by NMR ¹H, to understand why we did not observe changes in the UV/Vis spectrum.

Titration procedure

For the titration protocol, apart of MLG solutions in deuterated chloroform were prepared. These solutions were prepared with a concentration range of 0.003-0.005 M using 0.3mL of CDCl₃. MLGs 7 and 9 were dissolved in 0.1 mL of DMSO d₆ and measured using 0.3mL of CDCl₃. The solutions of pTsOH were prepared using two different concentrations, 0.05 M and 0.5M in 2.5mL of CDCl₃. Addition of pTsOH solution was performed using a micropipette and immediately recorded in a 500MHz NMR spectrophotometer and/or in 200 MHz NMR spectrophotometer.

Table S1. Calculated protonation constants K

| MLG | Macomber a | Local analysis b | Thordarson c |
|-----|------------|----------------|-------------|
| 7   | 122        | 182            | 109         |
| 8   | 54         | 86             | 20          |
| 9   | 71         | 31             | 21          |
| 10  | 940        | 914            | 1328        |
| 11  | 1518       | 1379           | 1210        |
| 12  | 248        | 178            | 120         |

aR. S. Macomber, J. Chem. Educ., 1992, 69, 375–378.
bP. Thordarson, Chem. Soc. Rev., 2011, 40, 1305–1323.
cD. B. Hibbert, P. Thordarson, Chem. Commun., 2016, 52, 12792–12805.
Figure S12. MLG 7 titration with pTsOH, recorded by NMR at 270 MHz in CDCl₃ at room temperature.
Figure S13. MLG 8 titration with pTsOH, recorded by NMR at 500 MHz in CDCl₃ at room temperature.
Figure S14. MLG 9 titration with pTsOH, recorded by NMR at 500 MHz in CDCl$_3$ at room temperature.
Figure S15. MLG 10 titration with pTsOH, recorded by NMR at 500 MHz in CDCl₃ at room temperature.
Figure S16. MLG 11 titration with pTsOH, recorded by NMR at 270 MHz in CDCl$_3$ at room temperature.
Figure S17. MLG 12 titration with pTsOH, recorded by NMR at 500 MHz in CDCl₃ at room temperature.
Figure S18. NMR nOe-dpfgse spectra of MLG E-11 with the offset 8.73ppm recorded at 500 MHz in CDCl₃ at room temperature.
Figure S19. NMR nOe-dpfgse spectra of MLG E-11 with the offset 8.52ppm recorded at 500 MHz in CDCl₃ at room temperature.
Figure S20. NMR nOe-dpfgse spectra of MLG E-11 with the offset 8.52ppm recorded at 500 MHz in CDCl₃ at room temperature.
**Figure S21.** NMR nOe-dpfgse spectra of MLG Z-12 with the offset 4.23ppm recorded at 500 MHz in CDCl₃ at room temperature.
Experimental determination of MLG operation

MLG operation process was studied using 0.002M solutions in CDCl₃ (for MLG 7 and 9 it was necessary to add 0.05mL of DMSO d₆). In several experiments, the solutions were prepared using 0.0015M of each MLG in CDCl₃:DMSO d₆ (3:0.2 volume relation). pTsOH was added to the same titration solutions. Irradiation of the solutions in the NMR tube was performed using an Aldrich® Micro Photochemical Reactor; it is important to highlight that the NMR tube had intimate contact with the LED. To support the NMR tube firmly, aluminum cans were used as shown in image S18. Two photoreactors were set in the experiments, one with LEDs of 435-445nm wavelength and other with LEDs of 400-410nm wavelength.

All spectra were recorded with a 500MHz NMR spectrophotometer at room temperature.

![Diagram of experimental setup](image)

**Figure S22.** Image of photoirradiation experiment.
Figure S23. $^1$H NMR spectrums of compounds $E-7$, $Z-7$, and $E-7H^+$. 
Figure S24. $^1$H NMR spectrums of compounds E-8, Z-8, and E-8H$^+$. 
Figure S25. $^1$H NMR spectrums of compounds E-9, Z-9, and E-9H$^+$. 
Figure S26. \(^1\)H NMR spectrums of compounds \(E-10\), \(Z-10\), and \(E-10H^+\).
Figure S27. $^1\text{H}$ NMR spectrums of compounds $E$-11, $Z$-11, and $E$-11H$^+$. 
MLG operation process

| Process | Molar Fraction | Molar Fraction | δH1 | δH1 |
|---------|----------------|----------------|------|------|
| E-7     | Z-7            | E-7            | Z-7  |
| Initial Mixture | 0.72 | 0.28 | 8.61 | 8.65 |
| 400nm x 10min | 0.35 | 0.65 | 8.61 | 8.65 |
| 12 eq. pTSOH | 0.65 | 0.35 | 8.7  | 8.77 |
| 15 eq. pTSOH | 0.75 | 0.25 | 8.72 | 8.81 |
| 400nm x 10min | 0.65 | 0.35 | 8.72 | 8.81 |
| 33,33 eq. TEA | 0.71 | 0.29 | 8.62 | 8.65 |
| 400nm x 10min | 0.39 | 0.61 | 8.62 | 8.65 |
| 33,33 eq. TEA | 0.87 | 0.13 | 8.62 | 8.65 |

**Figure S28.** Scheme of MLG 7 operation process.
Table S29. Molar Fraction of MLG 8 operation process.

| Entry | Molar Fraction | Molar Fraction | δH1 | δH1 |
|-------|----------------|----------------|------|------|
| 1     | Initial Mixture | 1 | 0 | 8.8 | 8.78 |
| 2     | 445nm x 10 min  | 0.48 | 0.52 | 8.8 | 8.78 |
| 3     | 400nm x 10 min  | 0.48 | 0.52 | 8.8 | 8.78 |
| 4     | 10 min          | 0.48 | 0.52 | 8.8 | 8.78 |
| 5     | 445nm x 10 min  | 0.71 | 0.29 | 9.17 | 9.36 |
| 6     | 400nm x 10 min  | 0.81 | 0.19 | 9.28 | 9.4 |
| 7     | 6.16 Eq. TEA    | 0.49 | 0.51 | 8.8 | 8.78 |

Figure S29. Scheme of MLG 8 operation process.
| Process                  | Molar Fraction | Molar Fraction | δH1  | δH1  |
|--------------------------|----------------|----------------|-------|-------|
| 1 Initial Mixture        | 0.85           | 0.15           | 8.65  | 8.63  |
| 2 400nm x 10 min         | 0.38           | 0.62           | 8.65  | 8.63  |
| 3 400nm x 10 min         | 0.34           | 0.64           | 8.65  | 8.63  |
| 4 tiempo 20 min          | 0.4            | 0.6            | 8.65  | 8.63  |
| 5 2.3 Eq. pTsOH          | 0.58           | 0.42           | 8.66  | 8.66  |
| 6 3.1 Eq. pTsOH          | 0.63           | 0.27           | 8.67  | 8.67  |
| 7 400nm x 10 min         | 0.6            | 0.4            | 8.67  | 8.67  |
| 8 13.3 Eq. TEA           | 0.78           | 0.22           | 8.65  | 8.63  |
| 9 400nm x 10 min         | 0.37           | 0.63           | 8.65  | 8.63  |
| 10 58 Eq. TEA            | 0.43           | 0.57           | 8.65  | 8.63  |
| 11 103 Eq. TEA           | 0.57           | 0.43           | 8.65  | 8.63  |
| 12 400nm x 10 min        | 0.51           | 0.49           | 8.65  | 8.63  |
| 13 445nm x 10 min        | 0.93           | 0.07           | 8.65  | 8.63  |
| 14 400nm x 10 min        | 0.52           | 0.48           | 8.65  | 8.63  |

**Figure S30.** Scheme of MLG 9 operation process.
| Entry | Process          | Molar Fraction | Molar Fraction | δH<sub>1</sub> | δH<sub>1</sub> |
|-------|------------------|----------------|----------------|----------------|----------------|
| 1     | Initial Mixture  | 0.82           | 0.18           | 8.83           | 8.8            |
| 2     | 400nm x 10 min   | 0.81           | 0.19           | 8.83           | 8.8            |
| 3     | 400nm x 10 min   | 0.39           | 0.61           | 8.83           | 8.8            |
| 4     | 1.5 Eq. pTsOH    | 0.55           | 0.45           | 9.19           | 9.37           |
| 5     | 3 Eq. pTsOH      | 0.8            | 0.2            | 9.31           | 9.42           |
| 6     | 400nm x 10 min   | 0.69           | 0.31           | 9.31           | 9.42           |
| 7     | 445nm x 10 min   | 1              | 0              | 9.31           | 9.42           |
| 8     | 7 Eq. TEA        | 1              | 0              | 8.82           | 8.7            |
| 9     | 400nm x 10 min   | 0.43           | 0.57           | 8.82           | 8.8            |

Figure S31. Scheme of MLG 10 operation process.
| Process | Molar Fraction E-11 | Molar Fraction Z-11 | Molar Fraction iso-11 | δH1 | δH1 |
|---------|---------------------|---------------------|-----------------------|------|------|
| 1 Initial Mixture | 1 | 0 | 0 | 8.84 | 8.75 |
| 2 445nm X 2min | 0.91 | 0.09 | 0 | 8.84 | 8.75 |
| 3 445nm X 5min | 0.87 | 0.13 | 0 | 8.84 | 8.75 |
| 4 445nm X 10min | 0.86 | 0.14 | 0 | 8.84 | 8.75 |
| 5 400nm x 20min | 0.83 | 0.11 | 0.05 | 8.84 | 8.75 |
| 6 1 Eq. TEA | 0.9 | 0.05 | 0.05 | 8.82 | 8.75 |
| 7 445nm X 10min | 0.24 | 0.71 | 0.05 | 8.82 | 8.75 |
| 8 445nm x 5min | 0.24 | 0.71 | 0.05 | 8.82 | 8.75 |
| 9 2 Eq. pTsOH | 0.93 | 0.02 | 0.05 | 9.09 | 9.09 |
| 10 2.5 Eq. TEA | 0.93 | 0.02 | 0.05 | 8.82 | 8.75 |
| 11 2.5 Eq. pTsOH | 0.93 | 0.02 | 0.05 | 8.89 | 8.89 |
| 12 445nm X 10min | 0.24 | 0.71 | 0.05 | 8.85 | 8.85 |
| 13 3 Eq. pTsOH | 0.35 | 0.6 | 0.05 | 8.89 | 8.89 |
| 14 3.5 Eq. pTsOH | 0.52 | 0.43 | 0.05 | 8.93 | 8.93 |
| 15 4 Eq. pTsOH | 0.6 | 0.35 | 0.05 | 8.98 | 8.98 |
| 16 4.5 Eq. pTsOH | 0.75 | 0.2 | 0.05 | 9.01 | 9.01 |
| 17 5 Eq. pTsOH | 0.79 | 0.16 | 0.05 | 9.05 | 9.05 |
| 18 445nm x 10 min | 0.56 | 0.39 | 0.05 | 9.02 | 9.02 |
| 19 5.5 Eq. pTSOH | 0.85 | 0.1 | 0.05 | 9.1 | 9.1 |
| 20 445nm x 10 min | 0.62 | 0.33 | 0.05 | 9.07 | 9.07 |
| 21 12 Eq. TEA | 0.77 | 0.18 | 0.05 | 8.82 | 8.75 |
| 22 445nm x 10 min | 0.2 | 0.75 | 0.05 | 8.81 | 8.74 |
Figure S32. Scheme of MLG 11 operation process.

Chart S1. Proposed molecule of $E$-12 decomposition by 400 nm light.
Figure S33. Scheme of MLG 12 operation process. Entry 2 and 5 correspond to the MLG 12 with visible light irradiation.
Description of Operation Process for MLG 8, 9, and 10.

The operation cycle of MLG 8 was tested starting with irradiation at 445 nm for 10 minutes where no response was observed. This was followed by irradiation at 400 nm for 10 minutes observing $E$ to $Z$ isomerization (entry 3, Scheme S2), followed by a second 10 min irradiation which had no effect on the isomer ratio (entry 4, Scheme S2). Next, the compound was irradiated at 445 nm for 10 minutes that led of $Z$ to $E$ isomerization where the $E$ isomer was the major product (entry 6, Scheme S2) followed by further irradiation of the $Z$ isomer at 400 nm 10 minutes (entry 7, Scheme S2). Then, two equivalents of pTsOH were added achieving $Z$ to $E$ reversal as confirmed by observation of the corresponding shifts in the NMR signals of both isomers (entry 8, Scheme S2). To verify that protonation slows down the isomerization of this MLG, the solution was irradiated at 400 nm light for 10 minutes observing minimal $E$ to $Z$ isomerization (entry 9, Scheme S2). The processes of entries 8 and 9 were repeated with the same isomerization pattern; the only difference was that when the 3.5 equivalents of pTsOH were added, the isomerization with 400 nm irradiation was minor in comparison with entry 9. To return to the initial isomer pattern, the solution was neutralized with 6.16 equivalents of triethylamine and irradiated with 400 nm light for 10 minutes to obtain the $Z$ isomer as major product (entry 13, Scheme S2), with a pattern similar to entry 3. Finally, irradiation was performed at 445 nm for 10 minutes to complete the function of MLG 8.
Scheme S1. Operation cycle of MLG 8. Each process was recorded by NMR at 500 MHz in CDCl₃ at room temperature. The concentration of MLG used in these experiments was 2 mM.
The study of MLG 9 started with irradiation of a solution with 400 nm light for 10 minutes to produce E to Z isomerization (entry 2, Scheme S3). To verify that the isomerization was caused by irradiation, the mixture with the Z isomer as main compound was irradiated with 400 nm light for 10 minutes, observing a slight increase of the compound (entry 3, Scheme S3). To the mixture with the Z isomer as the major isomer were added 2.3 equivalents of pTsOH to achieve Z to E isomerization. The first isomerization gave low proportion of the expected isomer, however, with additional 3.1 equivalents of pTsOH, an increase in the E isomer which was confirmed by a shift of the signals detected by NMR for both isomers (entries 5 and 6 Scheme S3). To verify the protonation effect, the sample was irradiated with 400 nm light for 10 minutes, and the isomerization decreased (entry 7, Scheme S3). With reference to the isomerization capability of MLG 9, the solution was neutralized with 13.3 equivalents of triethylamine, irradiated with 400 nm light for 10 minutes observing E to Z isomerization (entry 9, Scheme S3). It should be mentioned that up to 103 equivalents of triethylamine were added, and no effect was detected with the excess of the base. The isomerization was slowed down but without a significant response (entry 11, Scheme S3). After the addition of excess triethylamine, the solution was irradiated at 400 nm for 10 minutes, evidencing a E to Z isomerization pattern similar to entry 2. The solution was irradiated at 445 nm for 10 minutes, and Z to E isomerization was observed (entry 13, Scheme S3). Finally, E to Z transformation was attained with 400 nm light for 10 minutes (entry 14, Scheme S3) to close the operation cycle of MLG 9.
| Process                          | Molar Fraction | Molar Fraction | $\delta$H1 | $\delta$H1 |
|--------------------------------|----------------|----------------|-----------|-----------|
| 1 Initial Mixture              | 0.85           | 0.15           | 8.65      | 8.63      |
| 2 400nm x 10 min               | 0.38           | 0.62           | 8.65      | 8.63      |
| 3 400nm x 10 min               | 0.34           | 0.64           | 8.65      | 8.63      |
| 4 tiempo 20 min                | 0.4            | 0.6            | 8.65      | 8.63      |
| 5 2.3 Eq. pTsOH                | 0.58           | 0.42           | 8.66      | 8.66      |
| 6 3.1 Eq. pTsOH                | 0.63           | 0.27           | 8.67      | 8.67      |
| 7 400nm x 10 min               | 0.6            | 0.4            | 8.67      | 8.67      |
| 8 13.3 Eq. TEA                 | 0.78           | 0.22           | 8.65      | 8.63      |
| 9 400nm x 10 min               | 0.37           | 0.63           | 8.65      | 8.63      |
| 10 58 Eq. TEA                  | 0.43           | 0.57           | 8.65      | 8.63      |
| 11 103 Eq. TEA                 | 0.57           | 0.43           | 8.65      | 8.63      |
| 12 400nm x 10 min              | 0.51           | 0.49           | 8.65      | 8.63      |
| 13 445nm x 10 min              | 0.93           | 0.07           | 8.65      | 8.63      |
| 14 400nm x 10 min              | 0.52           | 0.48           | 8.65      | 8.63      |

**Scheme S2.** Operation cycle of MLG 9. Each process was recorded by NMR at 500 MHz in CDCl$_3$ at room temperature. The concentration of MLG used in these experiments was 2 mM.
The investigation of MLG 10 started with irradiation with 400 nm light for 20 minutes (to analyze and compare the effect of time with the same MLG and others) to achieve $E$ to $Z$ isomerization (entry 3, Scheme S4), giving the $Z$ compound as the main product. This mixture was treated with 3 equivalents of pTsOH until the $^1$H NMR signals shifted toward higher frequency, confirming $Z$ to $E$ isomerization (entry 5, Scheme S4). When the solution had the $E$ isomer as the major product, the effect of protonation by irradiation with 400 nm light for 10 minutes resulted in no further isomerization of the $Z$ isomer (entry 6, Scheme S4). Next, in our study, we tested the compound using 445 nm light and determined the complete transformation to the $E$ isomer (entry 7, Scheme S4). Subsequently, the solution was neutralized with 7 equivalents of triethylamine, and it was irradiated again with 400 nm light for 10 minutes, obtaining a high ratio of the $Z$ isomer (entry 9, Scheme S4), thus completing the operation cycle.
| Process                      | Molar Fraction | δH1   | δH1   |
|------------------------------|----------------|-------|-------|
| 1 Initial Mixture           | 0.82           | 8.83  | 8.8   |
| 2 400nm x 10 min            | 0.81           | 8.83  | 8.8   |
| 3 400nm x 10 min            | 0.39           | 8.83  | 8.8   |
| 4 1.5 Eq. pTsOH             | 0.55           | 9.19  | 9.37  |
| 5 3 Eq. pTsOH               | 0.8            | 9.31  | 9.42  |
| 6 400nm x 10 min            | 0.69           | 9.31  | 9.42  |
| 7 445nm x 10 min            | 1              | 9.31  | 9.42  |
| 8 7 Eq. TEA                 | 1              | 8.82  | 8.7   |
| 9 400nm x 10 min            | 0.43           | 8.82  | 8.8   |

**Scheme S3.** Operation cycle of MLG 10. Each process was recorded by NMR at 500 MHz in CDCl₃ at room temperature. The concentration of MLG used in these experiments was 2 mM.
**Table S2.** Summary of results for each process performed to verify MLGs 7 and 11.

| Process | Process Details | E-7 | Z-7 | δH | E-7 | Z-7 | δH | E-11 | Z-11 | δH | δH |
|---------|-----------------|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|
| 1       | Initial Mixture | 0.8 | 0.2 | 8.61 | 8.65 | 0.8 | 0.2 | 8.68 | 8.6 |
| 2       | 445nm X 10min   | 0.88 | 0.12 | 8.61 | 8.65 | 0.2 | 0.8 | 8.68 | 8.6 |
| 3       | 445nm X 10min   | 0.88 | 0.12 | 8.61 | 8.65 | 0.2 | 0.8 | 8.68 | 8.6 |
| 4       | 400nm x 7min    | 0.3 | 0.66 | 8.61 | 8.65 | 0.3 | 0.7 | 8.68 | 8.6 |
| 5       | 400nm x 7min    | 0.3 | 0.7 | 8.61 | 8.65 | 0.3 | 0.7 | 8.68 | 8.6 |
| 6       | 1 Eq. pTsOH     | 0.33 | 0.67 | 8.63 | 8.69 | 0.35 | 0.65 | 8.69 | 8.61 |
| 7       | 2 Eq. pTsOH     | 0.43 | 0.57 | 8.65 | 8.73 | 0.38 | 0.62 | 8.69 | 8.62 |
| 8       | 4 Eq. pTsOH     | 0.43 | 0.57 | 8.68 | 8.81 | 0.46 | 0.54 | 8.7 | 8.63 |
| 9       | 20 Eq. TEA      | 0.46 | 0.54 | 8.61 | 8.65 | 0.43 | 0.57 | 8.68 | 8.6 |
| 10      | 445nm x 10min   | 0.99 | 0.01 | 8.61 | 8.65 | 0.19 | 0.81 | 8.68 | 8.6 |
| 11      | 400nm x 7min    | 0.27 | 0.73 | 8.61 | 8.65 | 0.25 | 0.75 | 8.68 | 8.6 |
| 12      | 23 Eq. pTsOH    | 0.47 | 0.53 | 8.68 | 8.93 | 0.4 | 0.6 | 8.74 | 8.63 |
Figure S34. Scheme of MLG 7 and 11 operating in the same NMR tube.
Table S3. Summary of method of operation for the mixture of MLGs 7 and 11, outputs and corresponding labels

| Process | Output | Label |
|---------|--------|-------|
| 1       | I 0 II 0 III 0 IV 0 | a     |
| 2       | I 0 II 0 III 1 IV 1 | b     |
| 3       | I 0 II 0 III 1 IV 1 | b     |
| 4       | I 1 II 0 III 1 IV 1 | f     |
| 5       | I 0 II 1 III 0 IV 1 | F     |
| 6       | I 1 II 1 III 1 IV 1 | f-d   |
| 7       | I 1 II 1 III 1 IV 1 | f-d   |
| 8       | I 1 II 0 III 1 IV 0 | d     |
| 9       | I 0 II 0 III 0 IV 0 | k     |
| 10      | I 0 II 0 III 1 IV 0 | m     |
| 11      | I 0 II 1 III 0 IV 1 | p     |
| 12      | I 1 II 1 III 0 IV 0 | c     |
**Scheme S4.** Diagrams show how the logical operation is solved with MLGs 7 and 11 of each process carried out in the experiments with the theoretical labels. The concentrations of the two MLGs were 1.5 mM in CDCl₃:DMSO-d₆ (3:0.2 volume ratio), and NMR recorded each process at 500 MHz at room temperature.
| Process | E 7 | Z 7 | δH E 7 | Z 7 | E 10 | Z 10 | δH E 10 | Z 10 | E 11 | Z 11 | δH E 11 | Z 11 |
|---------|-----|-----|--------|-----|------|------|---------|------|------|------|---------|------|
| 1 Initial Mixture | 0.8 | 0.2 | 8.61 | 8.65 | 0.95 | 0.05 | 8.68 | 8.65 | 0.66 | 0.33 | 8.68 | 8.6 |
| 2 400nm x 5min | 0.46 | 0.54 | 8.61 | 8.65 | 0.63 | 0.37 | 8.68 | 8.65 | 0.52 | 0.48 | 8.68 | 8.6 |
| 3 400nm x 10min | 0.39 | 0.61 | 8.61 | 8.65 | 0.47 | 0.53 | 8.68 | 8.65 | 0.54 | 0.44 | 8.68 | 8.6 |
| 4 445nm x 5min | 0.86 | 0.14 | 8.61 | 8.65 | 0.66 | 0.34 | 8.68 | 8.65 | 0.28 | 0.72 | 8.68 | 8.6 |
| 5 445nm x 10min | 0.84 | 0.16 | 8.61 | 8.65 | 0.82 | 0.18 | 8.68 | 8.65 | 0.32 | 0.68 | 8.68 | 8.6 |
| 6 400nm x 15min | 0.34 | 0.66 | 8.61 | 8.65 | 0.47 | 0.53 | 8.68 | 8.65 | 0.54 | 0.46 | 8.68 | 8.6 |
| 7 0.7 Eq. pTsOH | 0.34 | 0.66 | 8.62 | 8.65 | 0.47 | 0.53 | 8.68 | 8.65 | 0.54 | 0.46 | 8.68 | 8.6 |
| 8 1.6 Eq. pTsOH | 0.38 | 0.62 | 8.64 | 8.66 | 0.49 | 0.51 | 8.69 | 8.66 | 0.6 | 0.4 | 8.69 | 8.6 |
| 9 3.3 Eq. pTsOH | 0.46 | 0.54 | 8.66 | 8.67 | 0.52 | 0.48 | 8.69 | 8.67 | 0.6 | 0.4 | 8.69 | 8.61 |
| 10 4 Eq. pTsOH | 0.58 | 0.42 | 8.67 | 8.67 | 0.64 | 0.36 | 8.69 | 8.67 | 0.62 | 0.37 | 8.69 | 8.61 |
| 11 7 Eq. pTsOH | 0.71 | 0.29 | 8.7 | 8.7 | 0.73 | 0.27 | 8.7 | 8.7 | 0.64 | 0.36 | 8.7 | 8.63 |
| 12 400nm x 10min | 0.71 | 0.29 | 8.7 | 8.7 | 0.6 | 0.4 | 8.7 | 8.7 | 0.64 | 0.36 | 8.7 | 8.62 |
| 13 10.5 Eq. pTsOH | 0.73 | 0.27 | 8.71 | 8.71 | 0.68 | 0.32 | 8.71 | 8.71 | 0.64 | 0.36 | 8.71 | 8.64 |
| 14 25 Eq. TEA | 0.73 | 0.27 | 8.61 | 8.65 | 0.68 | 0.32 | 8.68 | 8.65 | 0.64 | 0.36 | 8.68 | 8.6 |
| 15 400nm x 10min | 0.4 | 0.6 | 8.61 | 8.65 | 0.46 | 0.54 | 8.68 | 8.65 | 0.6 | 0.4 | 8.68 | 8.6 |
Figure S35. Scheme of operating process for MLG 7, 10 and 11 placed in the same NMR tube.
Table S5. Summary of method of operation for the mixture of MLGs 7, 10 and 11, outputs and corresponding labels

| Process     | Output | Label |
|-------------|--------|-------|
| I II III IV V VI | | |
| 1 Initial solution | 0 0 0 0 0 0 | a |
| 2 400nm x 5min | 0 1 0 0 0 0 | a-c |
| 3 400nm x 10min | 0 1 0 1 0 0 | c |
| 4 445nm x 5min | 0 0 0 0 1 0 | f1 |
| 5 445nm x 10min | 0 0 0 0 1 0 | f1 |
| 6 400nm x 15min | 0 1 0 1 0 0 | f2 |
| 7 0.7 Eq. pTsOH | 0 1 0 1 0 0 | f2-d |
| 8 1.6 Eq. pTsOH | 0 1 0 1 0 0 | f2-d |
| 9 3.3 Eq. pTsOH | 1 1 1 0 0 0 | f2-d |
| 10 4 Eq. pTsOH | 1 0 1 0 0 0 | f2-d |
| 11 7 Eq. pTsOH | 1 0 1 0 1 0 | d |
| 12 400nm x 10min | 1 0 1 0 1 0 | i |
| 13 10.5 Eq. pTsOH | 1 0 1 0 1 0 | d |
| 14 25 Eq. TEA | 0 0 0 0 0 0 | k |
| 15 400nm x 10min | 0 1 0 1 0 0 | n |
Scheme S5. Diagrams show how the logical operation is solved with MLGs 7, 10 and 11 of each process carried out in the experiments with the theoretical labels. The concentrations of the two MLGs were 1.5 mM in CDCl₃:DMSO-d₆ (3:0.2 volume ratio), and NMR recorded each process at 500 MHz at room temperature.

Theory calculation of MLG 7

The geometry structure of the MLGs that was used for the theoretical calculate, was the structure determined with NMR results and corroboration with literature molecules; and then the MLG series was refined used DFT b3lyp method with basis set 6-31 + g (d, p).

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

|   |   |   |   |
|---|---|---|---|
| C | -2.09232 | 3.41087 | -4.33503 |
| C | -1.29433 | 2.71497 | -5.25969 |
| C | -0.3024 | 1.84996 | -4.7963 |
| C | -0.15791 | 1.72399 | -3.41542 |
| C | -1.00783 | 2.46516 | -2.58634 |
| N | -1.96477 | 3.29965 | -3.00973 |
| H | 0.32892 | 1.2994 | -5.48943 |
| H | -2.86792 | 4.08723 | -4.68803 |
| H | -1.45717 | 2.85693 | -6.32373 |
| C | -0.68208 | 2.18107 | -1.15083 |
| C | 0.44861 | 1.19506 | -1.17089 |
| O | -1.22471 | 2.65425 | -0.16522 |
| C | 0.80877 | 0.88101 | -2.61172 |
| H | 1.84949 | 1.14397 | -2.84571 |
| H | 0.68996 | -0.18579 | -2.84577 |
| C | 0.96285 | 0.74665 | 0.00003 |
| H | 0.56101 | 1.09701 | 0.92776 |
| C | 2.12358 | -0.26543 | -0.00002 |
| C | 2.80431 | -0.85897 | -1.07216 |
The next part to obtain the theoretical absorption spectrum of E-7, was tested methods and basis set to find the better match of the experimental results with theoretical data. The screening was tested with 3 different DFT methods; b3lyp, b3pw91 and cam-b3lyp and the same basis set 3-21+g*, with b3lyp 3 different basis set 3-21+g*, 6-31+g(d), and Sto-3g. Accordingly with these data, the best method is the b3lyp with the 3-21+g* basis set and the solvation model ieppcm/CH3Cl.

Table S5. Comparation data of DFT methods for E-7 simulate UV/Vis absorption spectra

| Entry | Method | Basis set | Solvation | λ_{max} (nm) | f | ε (M^{-1} cm^{-1}) | Energy (eV) |
|-------|--------|-----------|------------|--------------|---|----------------|-------------|
| 1     | Experimental | - | CH3Cl | 400.35 | - | 20,200 | 3.0969 |
| 2     | b3lyp | 3-21+g* | - | 373.31 | 0.4288 | 17,000 | 3.3212 |
| 3     | b3lyp | 6-31+g(d) | ieppcm/CH3Cl | 399.74 | 0.5465 | 21,000 | 3.1016 |
| 4     | b3lyp | Sto-3g* | ieppcm/CH3Cl | 315.42 | 0.3793 | 15,000 | 3.9307 |
| 5     | b3pw91 | 3-21+g* | ieppcm/CH3Cl | 397.17 | 0.5474 | 21,000 | 3.1217 |
| 6     | cam-b3lyp | 3-21+g* | ieppcm/CH3Cl | 340.81 | 0.6748 | 27,000 | 3.6379 |
Figure S37. Theory UV/Vis absorption spectra, and data. Method b3lyp with the 3-21+g* basis set and the solvation model iefpcm/CH$_3$Cl.

Figure S38. a) Orbital $\pi$ that correspond of MLG $E$-7 HOMO. b) Orbital $\pi^*$ that correspond of MLG $E$-7 LUMO. c) MO that have n orbital of MLG $E$-7.