

## Multifunctional switching of a photo- and electro-chemiluminescent Iridium complex

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**ELECTRONIC SUPPLEMENTARY INFORMATION**

## 1. Materials and Methods

**Solvents and reactants.** The synthesis and characterization of compound **1-o,o** was reported elsewhere.<sup>S1</sup> Dichloromethane and tetrahydrofuran (Merck Uvasol), tetrabutylammonium hexafluorophosphate (TBAP, Fluka, >99%), tripropylamine (Aldrich, >98%), tributylamine (Fluka, >99.5%), and trifluoromethanesulfonic acid (CF<sub>3</sub>SO<sub>3</sub>H, Aldrich, >99%) were used as received.

**Absorption and luminescence spectroscopy.** Absorption spectra were recorded with a Perkin Elmer Lambda 45 or Varian Cary 50 spectrophotometers. Luminescence spectra were obtained with a Perkin Elmer LS50 spectrofluorimeter. Quartz cells with 1 cm optical path length were used. Dilute solutions were used in order to minimize inner filter effects. The experimental errors are ±1 nm for the wavelengths and ±10% for the absorption and luminescence intensities.

**Photochemistry.** The solutions were irradiated in a 3-mL quartz cell and kept under continuous stirring. Irradiation experiments in the UV were performed using a medium pressure Hg lamp (Hanau Q400, 150 W); the emission lines at either 330 or 365 nm were isolated by means of interference filters. The photon flux at 365 nm referred to the volume of 1 L, measured by ferrioxalate actinometry,<sup>S2</sup> was  $1.333 \times 10^{-6}$  Einstein s<sup>-1</sup>. Irradiation in the visible region was performed with the 250 W halogen lamp of a slide projector, using an interference filter to select the desired wavelength (590 nm). The photon flux at 590 nm referred to the volume of 1 L, measured by the potassium reineckate actinometer,<sup>S2</sup> was  $3.44 \times 10^{-5}$  Einstein s<sup>-1</sup>.

**Voltammetric experiments.** Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) scans were carried out on argon-purged tetrahydrofuran or dichloromethane solutions at concentrations of ca.  $5 \times 10^{-4}$  M and with 0.05 M tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte. CV and DPV experiments were performed with an Autolab 30 multipurpose instrument interfaced to a PC using a platinum disk (0.12 cm<sup>2</sup>) as the working electrode, a Pt spiral as the counter electrode, and an Ag wire as a quasi-reference electrode. The reversible oxidation wave of ferrocene ( $E_{1/2} = +0.57$  V vs SCE in THF and +0.51 V in CH<sub>2</sub>Cl<sub>2</sub>)<sup>S3</sup> was used as an internal reference for the potential values. CV scans were obtained with sweep rates in the range 20–500 mV s<sup>-1</sup>, while the DPV experiments were performed with a scan rate of 20 mV s<sup>-1</sup>, a pulse height of 75 mV, and a pulse duration of 40 ms. For reversible processes, the halfwave potential values were obtained from the CV patterns; in the case of irreversible process the potential

value of the corresponding DPV peak was considered. The errors on the redox potential values are estimated to be  $\pm 10$  mV for reversible processes and  $\pm 20$  mV for irreversible processes.

**Electrochemiluminescence.** ECL spectra were recorded in an argon-purged  $\text{CH}_2\text{Cl}_2/\text{TBAP}$  solution ( $3 \times 10^{-4}$  M) in the presence of tripropylamine (0.3 M) as a co-reactant.<sup>S4</sup> The cell was a quartz cuvette of 1 cm pathlength equipped with three electrodes. The working electrode was a platinum disc (4 mm diameter) located parallel to one of the cell windows. The counter electrode was a platinum spiral and a silver wire was used as a quasi-reference electrode. The ECL spectra were obtained during a chronoamperometry at +1.0 V (vs SCE) for 20 ms. The chronoamperometry was obtained using an Autolab 30 potentiostat, while the light signal was recorded by a Cary Eclipse spectrofluorimeter. The voltage applied to the photomultiplier tube was 800 V, the slits were fixed at 20 nm and the scan rate was 200 nm/min.

## 2. Determination of the photoreaction quantum yields

The quantum yields of the ring-closing ( $\Phi_{o \rightarrow c}$ ) and ring-opening ( $\Phi_{c \rightarrow o}$ ) photoreactions were determined by spectrophotometry by means of a previously reported method for the kinetic treatment of photoreversible systems.<sup>S5</sup>

Equation S1 describes the color-forming (i.e., ring-closing) kinetics when the irradiation is performed at an isosbestic wavelength (in our case, 365 nm)

$$dA_c/dt = \epsilon_c \times \Phi_{o \rightarrow c} I^0 F A^0 - A_c [I^0 F \epsilon_{iso} (\Phi_{o \rightarrow c} + \Phi_{c \rightarrow o})] \quad (\text{S1})$$

in which  $A_c$  and  $\epsilon_c$  are the absorbance and the molar absorption coefficient of the closed (colored) form at the analyzed wavelength (in our case, 650 nm);  $I^0$  is the intensity of the irradiating light (photon flux values were determined by chemical actinometry as reported above),  $A^0$  and  $\epsilon_{iso}$  are the absorbance and the molar absorption coefficient at the irradiation (isosbestic) wavelength.  $F$  is the photokinetic factor,  $F = (1 - 10^{-A_{\text{total}}})/A_{\text{total}}$ .<sup>S6</sup>

From equation S1 and absorbance-time data sets (Figure S1),  $(\Phi_{o \rightarrow c} + \Phi_{c \rightarrow o})$  and  $\epsilon_c \times \Phi_{o \rightarrow c}$  could be determined from the slope and intercept of the linear plots of  $dA_c/dt$  vs  $A_c$  (Figure S2).<sup>S5</sup>

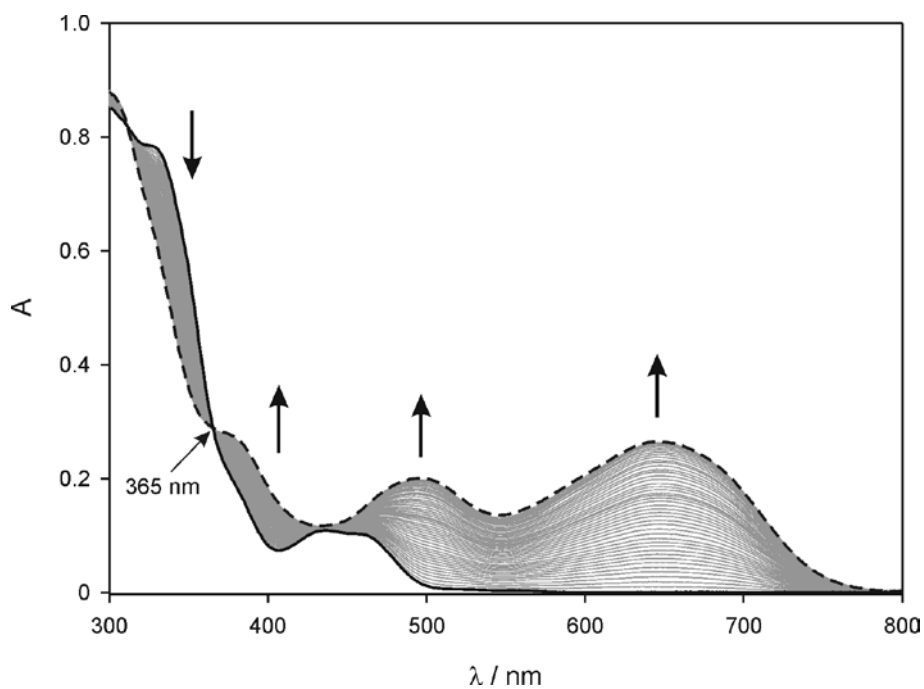
Equation S2 was used to describe the kinetics of the ring-opening reaction caused by visible light irradiation (Figure S3). In this equation,  $A_c'$  is the absorbance of the colored form at the irradiation wavelength (in our case, 590 nm).

$$-dA_c'/dt = \epsilon_c \times \Phi_{c \rightarrow o} I^0 (1 - 10^{-A_c'}) \quad (\text{S2})$$

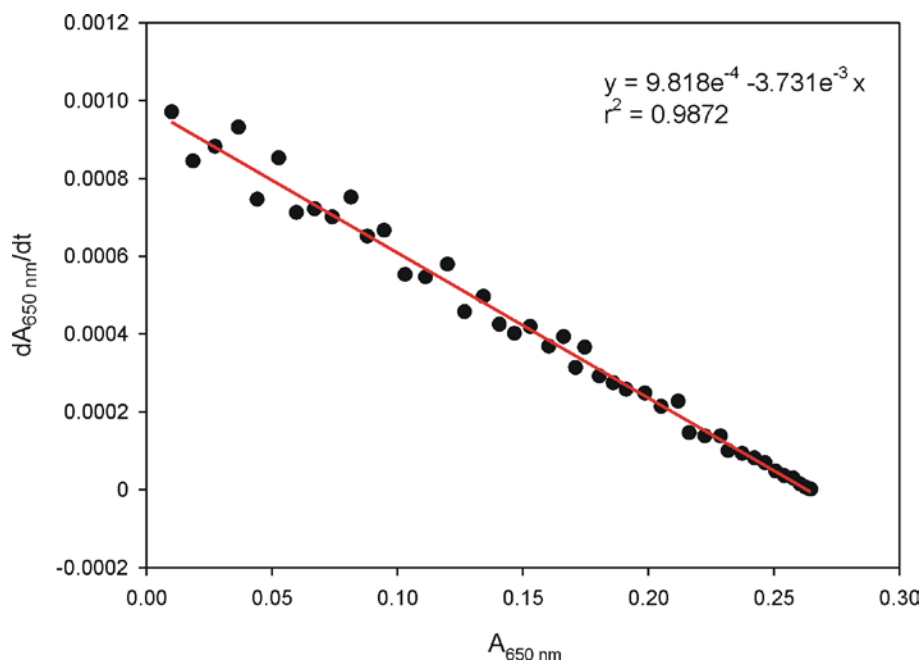
The linear plot of  $dA_c'/dt$  vs  $10^{-A_c'}$  (Figure S4) gives  $\epsilon_c \times \Phi_{c \rightarrow o} \times I^0$  from both the intercept and slope. Combining the results from equations S1 and S2, the photochemical and spectral parameters of the system were obtained. The uncertainty in the quantum yield determination was  $\pm 20\%$ .

The composition of the photostationary state obtained upon irradiation at an isosbestic wavelength (in our case, 365 nm, at which  $\epsilon_o = \epsilon_c$ ) was determined by equation S3:

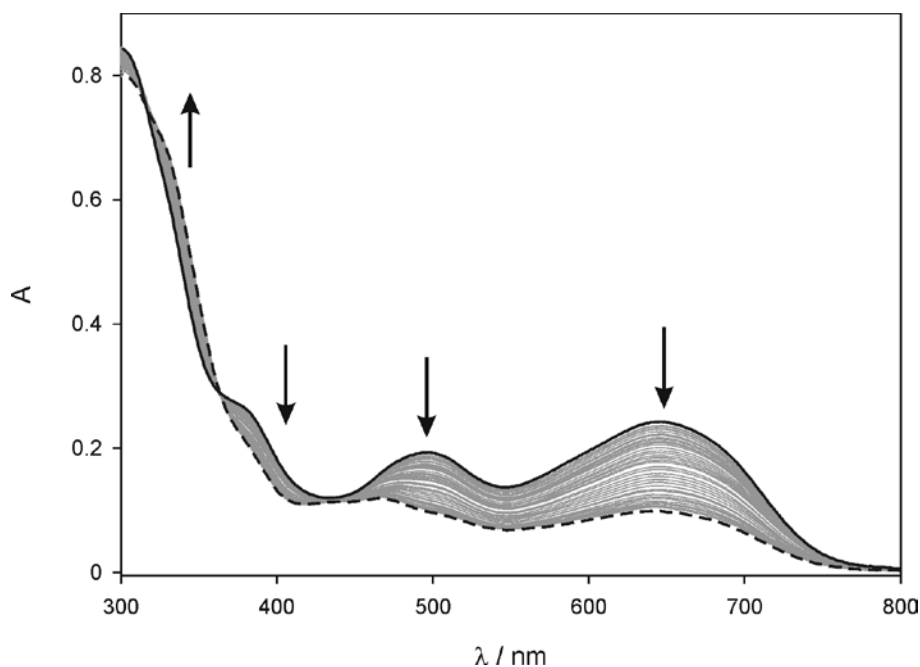
$$([c]/[o])_{\text{PSS}} = \Phi_{o \rightarrow c} / (\Phi_{o \rightarrow c} + \Phi_{c \rightarrow o}) \quad (\text{S3})$$



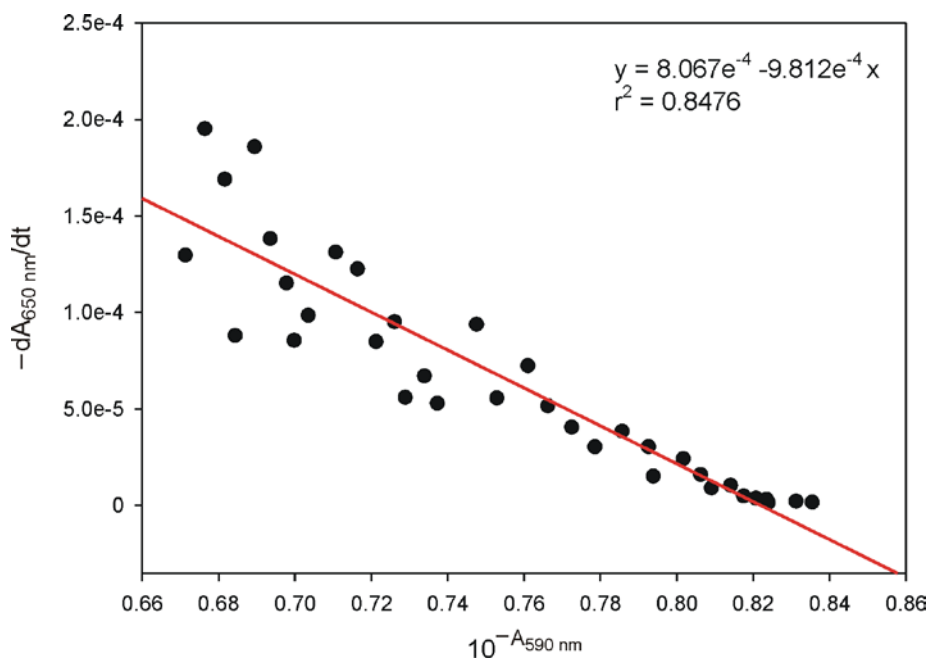
**Figure S1.** Absorption spectral changes observed upon irradiation at 365 nm of **1-o,o** ( $1.9 \times 10^{-5}$  M) in THF at room temperature. The final irradiation time was 42 min.



**Figure S2.** Plot of  $dA/dt$  as a function of the absorbance at 650 nm; the data are extracted from the absorption spectra shown in Figure S1. The red line represents the data fit according to equation S1.

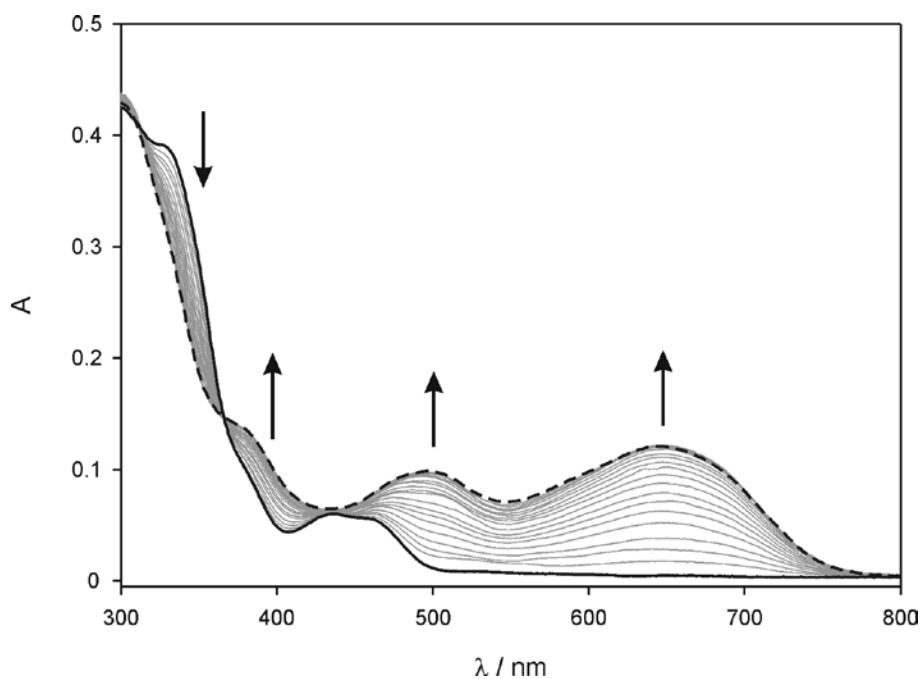


**Figure S3.** Absorption spectral changes observed upon irradiation at 590 nm of the solution obtained by exhaustive irradiation of **1-o,o** ( $1.9 \times 10^{-5}$  M) at 365 nm (see Figure S1). The final irradiation time was 190 min.

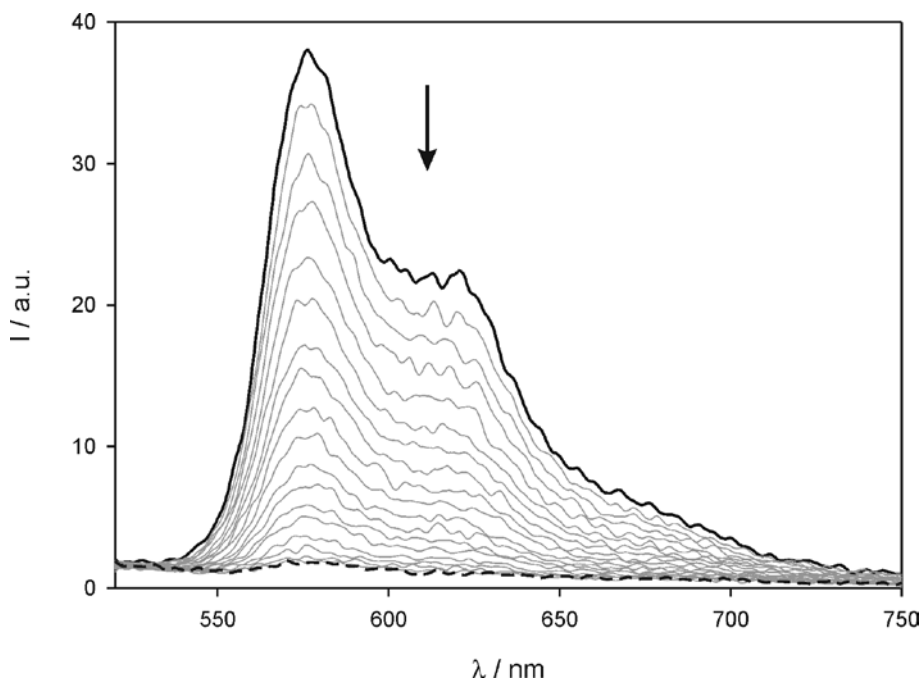


**Figure S4.** Plot of  $-dA/dt$  at 650 nm as a function of  $10^{-A_{590 \text{ nm}}}$ ; the data are extracted from the absorption spectra shown in Figure S3. The red line represents the data fit according to equation S2.

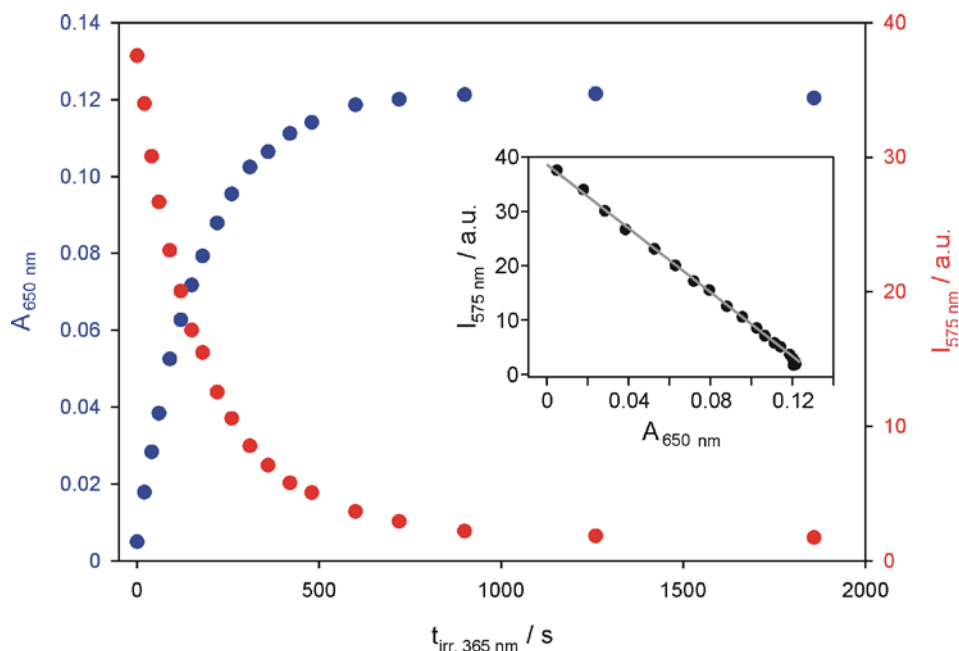
### 3. Absorption and luminescence changes upon photocyclization



**Figure S5.** Absorption spectral changes observed upon irradiation of **1-o,o** ( $1.0 \times 10^{-5}$  M) at 365 nm in THF at room temperature.

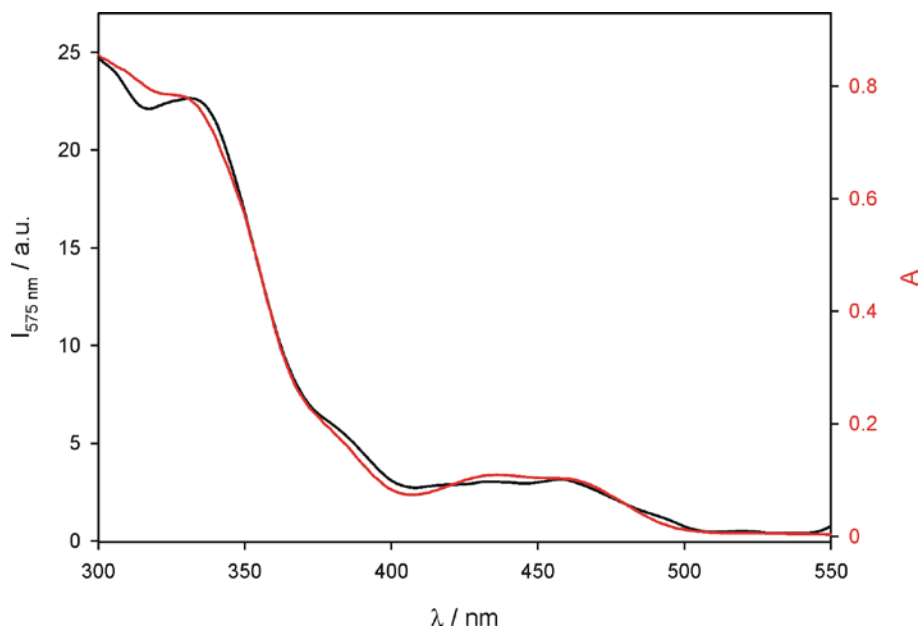


**Figure S6.** Luminescence spectral changes ( $\lambda_{exc} = 365$  nm) observed upon irradiation of **1-o,o** ( $1.0 \times 10^{-5}$  M) at 365 nm in THF at room temperature.



**Figure S7.** Plot of the absorbance at 650 nm (blue) and the emission intensity ( $\lambda_{\text{exc}} = 365 \text{ nm}$ ) at 575 nm (red) as a function of the irradiation time at 365 nm. The inset shows the linear correlation between the absorption and luminescence changes.

#### 4. Luminescence excitation spectrum of 1-o,o



**Figure S8.** Excitation (black,  $\lambda_{\text{em}} = 575 \text{ nm}$ ) and absorption (red) spectra of **1-o,o** in THF at room temperature. The excitation spectrum was recorded on a solution exhibiting a low absorbance (< 0.1) in the investigated spectral region, and its shape is therefore quantitatively comparable with that of the absorption spectrum.



## References

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