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Electronic Supplementary Information

Ureasil Organic-Inorganic Hybrids as Photoactive Waveguides for Conjugated Polyelectrolyte Luminescent Solar Concentrators

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1. Instrumentation

Fourier transform infrared (FTIR) measurements were carried out on a Perkin-Elmer spectrum 100 FTIR spectrometer at room temperature and collected over a range of 400-4000 cm^{-1} by averaging 64 scans at a resolution of 4 cm^{-1}. The grounded samples (2 mg) were mixed with potassium bromide (175 mg) and pressed into pellets. The contributions to the Amide I band (1600-1800 cm^{-1}) were obtained through spectral deconvolution using Gaussian band fitting in Origin 8.0s (Microcal).

Steady-state photoluminescence (PL) measurements were carried on a Fluorolog-3 spectrophotometer (Horiba Jobin Yvon), using the front-face configuration for solid-state samples. Emisson and excitation slits were fixed at 0.75 nm. Photoluminescence quantum yields were measured in a F-3018 integrating sphere accessory mounted on a FluoroMax-4 spectrophotometer (Horiba Jobin Yvon) and the values reported are the mean of three repeat measurements. The method is accurate to within 10%. Emission and excitation spectra were corrected for the wavelength response of the system and the intensity of the lamp profile over the excitation range, respectively, using correction factors supplied by the manufacturer. UV/Vis absorption spectra were recorded using a Perkin Elmer Lambda 1050 UV/Vis scanning spectrometer. Fluorescence decays were measured using the picosecond time-correlated single photon counting (TCSPC) method at the Collaborative Optical Spectroscopy, Micromanipulation and Imaging Centre (COSMIC), University of Edinburgh, U.K. The excitation source was the second harmonic of the pulse-picked output of a Ti-Sapphire femtosecond laser system (Coherent, 10 W Verdi and Mira Ti-Sapphire), delivering pulses of ≈200 fs at 4.75 MHz repetition rate. Fluorescence decays were measured using an Edinburgh Instruments spectrometer equipped with TCC900 photon counting electronics. The instrument response of the system was ≈90 ps full-width-half-maximum (FWHM). The decay curves were analysed using a standard iterative reconvolution method, assuming a multi-exponential decay function. Reconvolution and fitting of the fluorescence decays were carried out using Globals WE software package. The quality of fit was judged on the basis of the reduced chi-square statistic, χ^2, and the randomness of residuals.

2. Steady-State Photoluminescence Studies

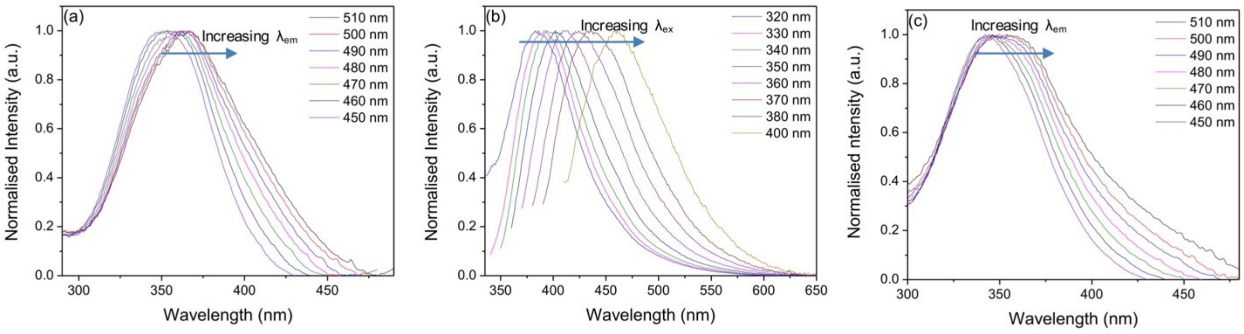


Figure S1. Excitation spectra of (a) **DU-CPE-0** and (c) **TU-CPE-0** at different emission wavelengths. Emission spectra of (b) **TU-CPE-0** at different excitation wavelengths.

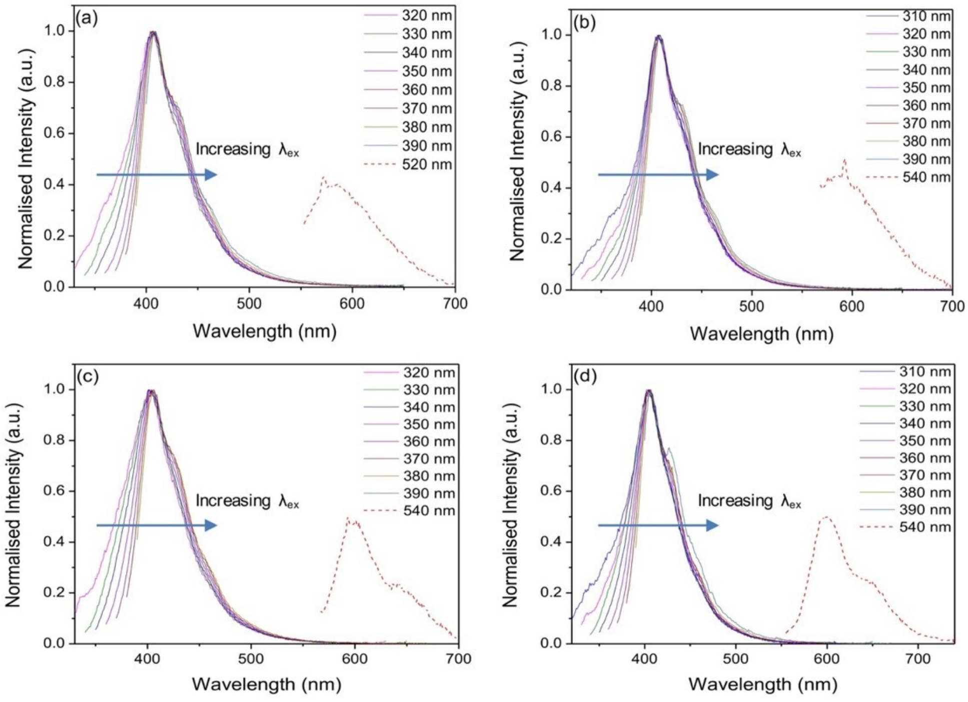


Figure S2. Emission spectra of (a) **DU-CPE-02**, (b) **DU-CPE-04**, (c) **TU-CPE-02** and (d) **TU-CPE-04** at different excitation wavelengths.

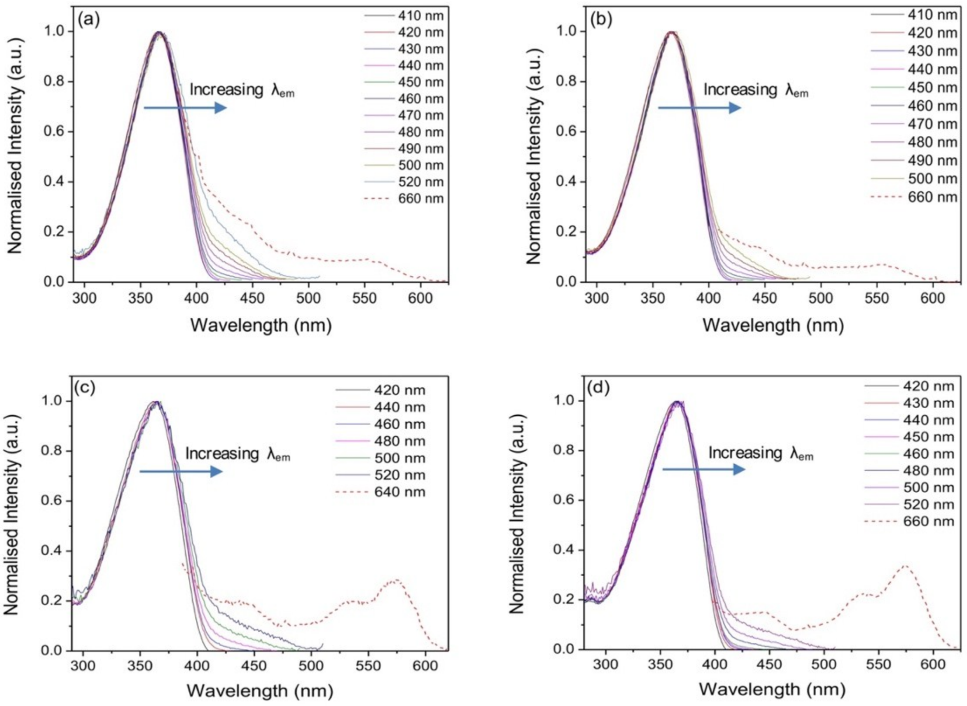


Figure S3. Excitation spectra of (a) **DU-CPE-02**, (b) **DU-CPE-04**, (c) **TU-CPE-02** and (d) **TU-CPE-04** at different emission wavelengths.

3. FTIR Spectroscopy in the Amide I Region

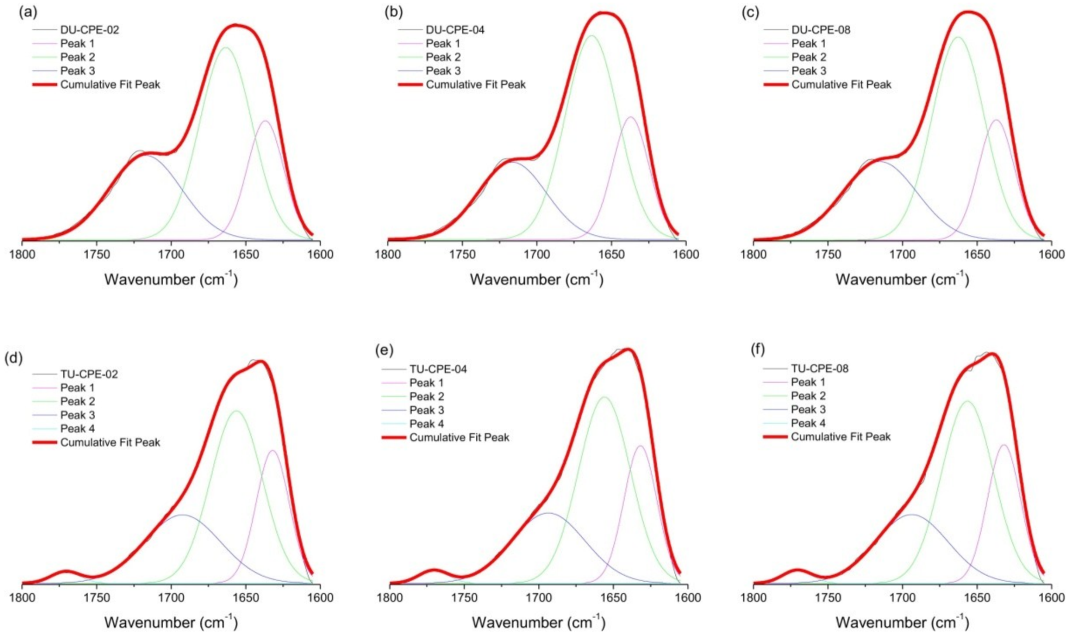


Figure S4. FTIR spectra and corresponding Gaussian curve-fits of the Amide I region of (a) **DU-CPE-02**, (b) **DU-CPE-04**, (c) **DU-CPE-08**, (d) **TU-CPE-02**, (e) **TU-CPE-04** and (f) **TU-CPE-08**.

Table S1. Results of Gaussian curve fitting of the Amide I band of **DU-CPE-*x*** and **TU-CPE-*x***, showing the peak position, area and % contribution for each component resolved.

Sample ID	**Peak 1 /cm^{-} Contribution (%)**	**Peak 2 /cm^{-1} Contribution (%)**	**Peak 3 /cm^{-1} Contribution (%)**	**Peak 4 /cm^{-1} Contribution (%)**
DU-CPE-0	1637.1 (21.8)	1663.3 (47.9)	1715.4 (30.3)	
DU-CPE-02	1636.8 (21.1)	1663.3 (49.3)	1717.4 (29.6)	
DU-CPE-04	1637.0 (21.7)	1663.2 (52.7)	1716.5 (25.6)	
DU-CPE-08	1637.0 (20.7)	1662.7 (51.2)	1715.2 (28.1)	
TU-CPE-0	1632.1 (22.8)	1656.2 (46.7)	1692.7 (28.6)	1770.6 (1.9)
TU-CPE-02	1631.9 (23.3)	1656.2 (47.3)	1692.4 (27.6)	1770.9 (1.8)
TU-CPE-04	1631.9 (23.0)	1656.0 (49.0)	1693.6 (26.1)	1770.6 (1.9)
TU-CPE-08	1631.9 (23.7)	1656.4 (48.8)	1693.8 (25.6)	1770.8 (1.9)

4. Picosecond (ps) Time-Correlated Single Photon Counting (TCSPC) Studies

4.1 Fitting procedure

Fluorescence decays were measured for **PBS-PFP-PDI** in solution (1:1 v/v water:1,4-dioxane) and for DU-CPE-*x* and TU-CPE-x samples upon excitation at 370 nm and detection of the emission at 420 nm, 500 nm and 600 nm. For all samples, the decay curves displayed complex multi-exponential behaviour, requiring either two, three or four components to fit the experimental data. The form of the theoretical multi-exponential decay was fitted using the following model:

$$I(t) = \sum_i \alpha_i exp(-t/\tau_i) \qquad (1)$$

where α_i and τ_i are the pre-exponential factor and characteristic lifetime for component *i*, respectively. This theoretical expression takes into account the response of a sample upon an infinitely sharp excitation, also known as a δ-function.[4] In this model, the intensity is assumed to decay as the sum of individual single exponential decays. When studying one fluorophore presenting a complex decay, it is generally acceptable to consider that such fluorophore presents the same radiative decay rate in each environment. Thus, in this case α_i represents the fraction of molecules in each environment at $t = 0$.[5]

The average fluorescence lifetime $<\tau>$ is calculated from:

$$< \tau >= \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i} \qquad (2)$$

In practise however, the excitation pulse is not infinitely short and thus the sample does not only decay starting directly after the pulse. Thus, the theoretical multi-exponential decay model (1) is reconvoluted with the instrumental response function (IRF) (which includes the width of the excitation pulse and possible electronic responses of the instrument) using the following integral:

$$I'(t) = \int_0^t E(t')I(t - t')dt' \qquad (3)$$

where $E(t)$ is the excitation pulse and $I(t)$ is the theoretical decay model (1). This expression states that the experimentally-measured intensity at time t is given by the sum of the intensities expected for all δ-function excitation pulses that occur until time t, if the excitation pulse is imagined to be comprised as a series of δ-functions with different amplitudes.[6] This model is then fit to the measured decay through the method of non-linear least squares analysis (NLLS), which tests if the used model is consistent with the data. This is achieved by varying α_i and τ_i until the goodness-of-fit parameter, χ^2 is at a minimum. χ^2 is described by:

$$\chi^2 = \sum_{i=1}^{n} \left[\frac{y_i - f_{ic}}{y_i^2} \right]^2 \qquad (4)$$

where y_i is the measured data, n is the number of data points and f_{ic} is the calculated fit.

The quality of the NLLS analysis was also judged based on the randomness of the weighted residuals plot.

4.2 Supplementary Decay Curves and Fits

λ_{ex} = 466 nm	τ_1/ns	τ_2/ns	τ_3/ns	α_1	α_2	α_3	χ^2
λ_{em} = 600 nm	0.001	1.596	5.461	0.927	0.022	0.051	1.25

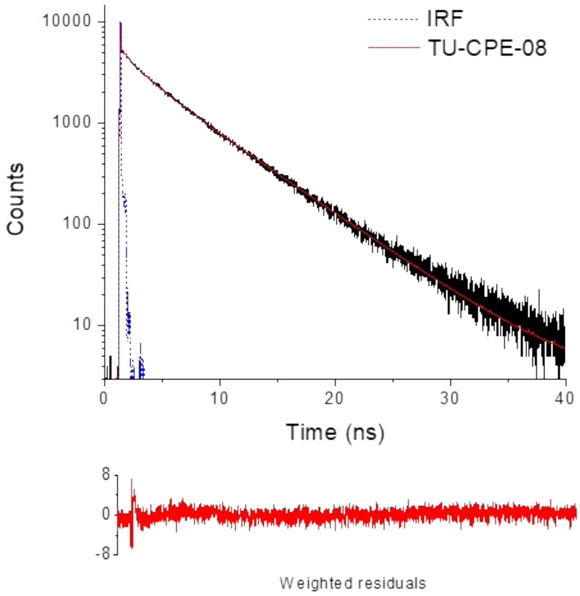


Figure S5. Emission decay curve (solid black line) and corresponding fit (solid red line) for **TU-CPE-08** (λ_{ex} = 466 nm, λ_{em}= 600 nm). The fitted decay times (τ_i), the pre-exponential coefficients (α_i), chi-squared (χ^2), weighted residuals and instrument response function (IRF, dotted blue line) are also shown.

Table S2. Photoluminescence lifetimes (τ_i), pre-exponential coefficients (α_i), and chi squared (χ^2) values obtained from fitting of the emission decays (λ_{ex} = 370 nm) at λ_{em} = 420 and 500 nm.

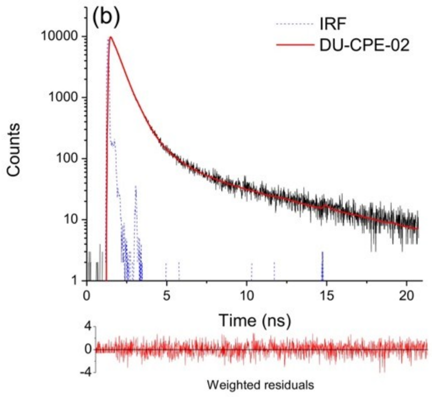
λ_{em} = 420 nm

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	α_1	α_2	α_3	α_4	χ^2
CPE	0.026±0.001	0.553±0.002	1.072±0.020		-0.899±0.001	0.947±0.001	0.053±0.001		1.14
DU-CPE-0		0.47±0.01	2.56±0.04	10.08±0.12		0.75 ±0.02	0.20 ± 0.01	0.05 ± 0.01	1.55
DU-CPE-02	0.029±0.005	0.538±0.002	1.640±0.037		-0.281±0.004	0.982±0.002	0.018±0.001		1.03
DU-CPE-04		0.537±0.002	1.545±0.068		0.990±0.002	0.010±0.001			1.32
DU-CPE-08		0.548±0.002	1.224±0.045		0.983±0.002	0.017±0.001			1.20
TU-CPE-0		0.522±0.030	4.204±0.052	12.740±0.089		0.474±0.005	0.378±0.003	0.148±0.001	1.43
TU-CPE-02		0.513±0.003	1.050±0.029	8.103±0.025		0.943±0.003	0.052±0.002	0.005±0.001	1.12
TU-CPE-04		0.544±0.003	5.396±0.187			0.995±0.003	0.005±0.001		1.25
TU-CPE-08		0.550±0.003	3.223±0.141			0.996±0.003	0.004±0.001		1.308

λ_{em} = 500 nm

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	α_1	α_2	α_3	α_4	χ^2
CPE	0.034±0.003	0.582±0.002	1.364±0.028		-0.491±0.002	0.967±0.016	0.033±0.001		1.07
DU-CPE-0		0.39 ± 0.02	2.79 ± 0.05	10.90 ± 0.14		0.63 ± 0.03	0.29 ± 0.02	0.07 ± 0.02	1.66
DU-CPE-02	0.041±0.003	0.556±0.004	1.431±0.025	6.980±0.191	-0.184±0.001	0.941±0.001	0.052±0.001	0.007±0.001	0.99
DU-CPE-04	0.022±0.003	0.597±0.004	4.106±0.116		-0.782±0.002	0.989±0.001	0.011±0.001		1.25
DU-CPE-08	0.024±0.003	0.618±0.004	3.624±0.112		-0.732±0.002	0.991±0.002	0.009±0.001		1.18
TU-CPE-0		0.792±0.030	4.845±0.052	14.213±0.102		0.425±0.005	0.431±0.003	0.144±0.001	1.24
TU-CPE-02		0.593±0.006	1.904±0.037	10.390±0.167		0.873±0.004	0.112±0.002	0.015±0.001	1.32
TU-CPE-04		0.563±0.003	2.125±0.087	9.297±0.204		0.957±0.002	0.030±0.001	0.013±0.001	1.49
TU-CPE-08		0.605±0.007	1.504±0.030	8.819±0.240		0.840±0.004	0.153±0.003	0.007±0.001	1.32

τ_1/ns	τ_2/ns	τ_3/ns	τ_4/ns	α_1	α_2	α_3	α_4	χ^2
0.04	0.56	1.43	6.98	-0.18	0.94	0.05	0.01	0.99



τ_1/ns	τ_2/ns	τ_3/ns	α_1	α_2	α_3	χ^2
0.02	0.60	4.11	-0.78	0.99	0.01	1.25

τ_1/ns	τ_2/ns	τ_3/ns	α_1	α_2	α_3	χ^2
0.02	0.62	3.62	-0.73	0.99	0.01	1.18

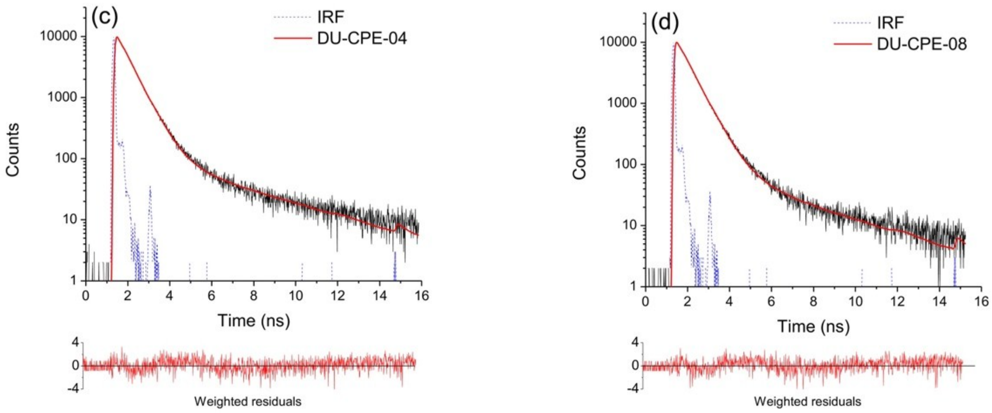
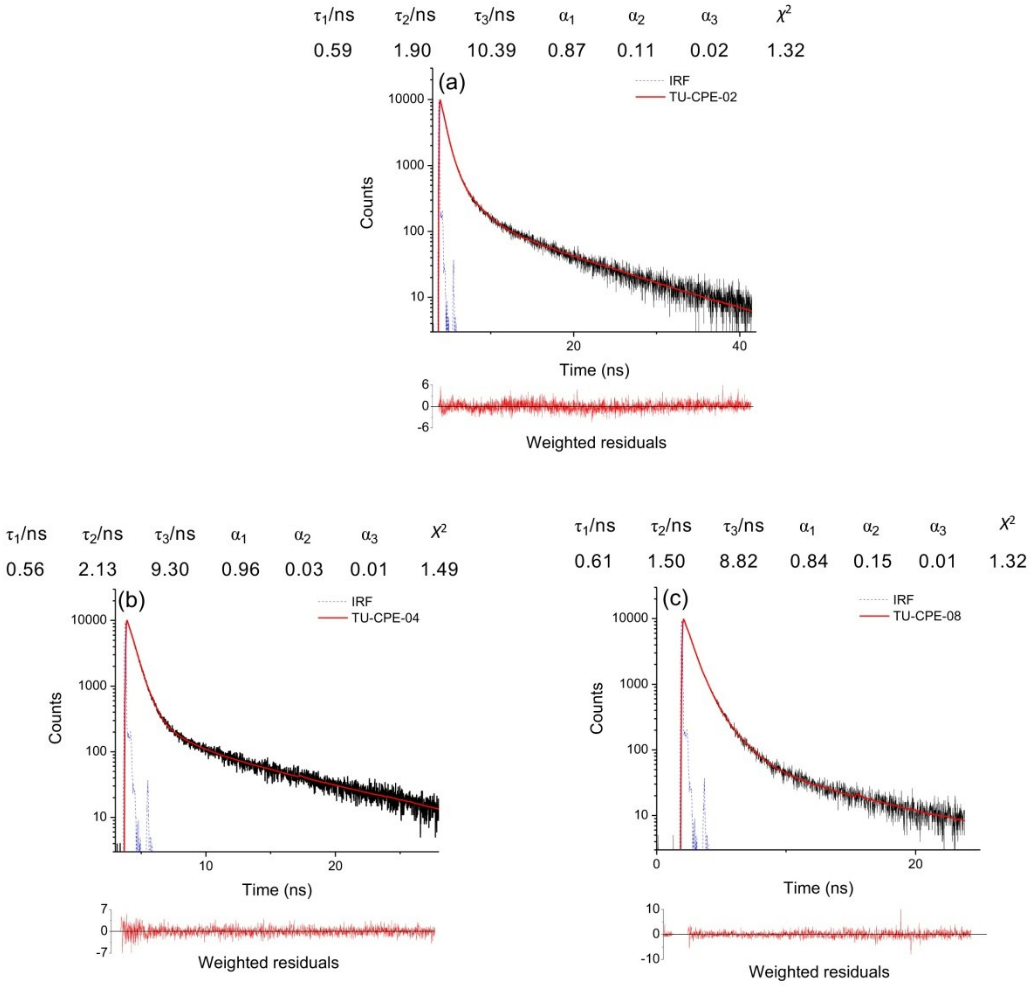


Figure S6. Emission decay curves (solid black lines) and corresponding fits (solid red lines) for (a) **DU-CPE-02**, (b) **DU-CPE-04** and (c) **DU-CPE-08** upon excitation at 370 nm (λ_{em} = 500 nm). The fitted decay times (τ_i), the pre-exponential coefficients (α_i), chi-squared (χ^2), weighted residuals and instrument response function (IRF, dotted blue line) are also shown.



(a)

τ_1/ns	τ_2/ns	τ_3/ns	α_1	α_2	α_3	χ^2
0.59	1.90	10.39	0.87	0.11	0.02	1.32

(b)

τ_1/ns	τ_2/ns	τ_3/ns	α_1	α_2	α_3	χ^2
0.56	2.13	9.30	0.96	0.03	0.01	1.49

(c)

τ_1/ns	τ_2/ns	τ_3/ns	α_1	α_2	α_3	χ^2
0.61	1.50	8.82	0.84	0.15	0.01	1.32

Figure S7. Emission decay curves (solid black lines) and corresponding fits (solid red lines) for (a) **TU-CPE-02**, (b) **TU-CPE-04** and (c) **TU-CPE-08 upon** excitation at 370 nm (λ_{em} = 500 nm). The fitted decay times (τ_i), the pre-exponential coefficients (α_i), chi-squared (χ^2), weighted residuals and instrument response function (IRF, dotted blue line) are also shown.

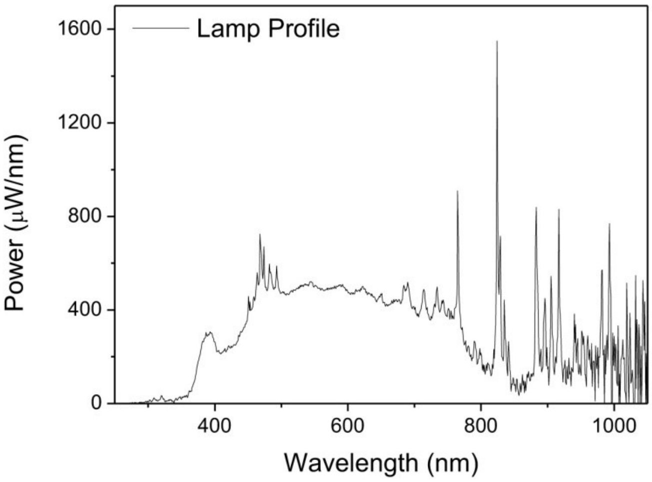


Figure S8. Optical power spectrum of the solar simulator (AM1.5G).

5. References

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