Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Photoinduced Interfacial Charge Separation Dynamics in Zeolitic Imidazolate Framework

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Supplemental Figures:

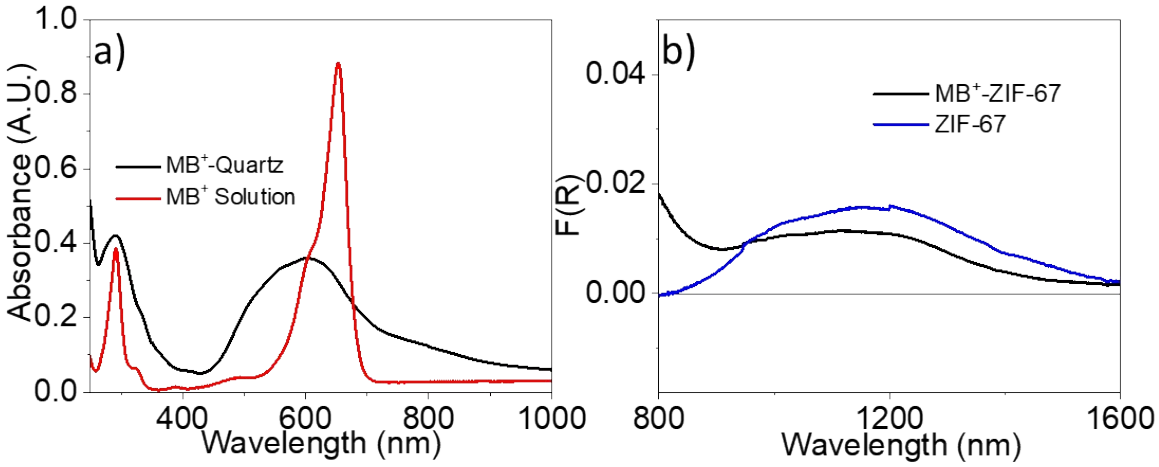

Figure S1. (a) UV-Visible spectra comparing MB^+-Quartz to MB^+ in methanolic solution demonstrating the spectrum broadening effect for aggregated MB^+. (b) Enlarged NIR region showing the presence of the lower-lying [$^4A_2(F)$-$^4T_1(F)$] transition in the MB^+ sensitized ZIF-67 sample compared to bare ZIF-67.

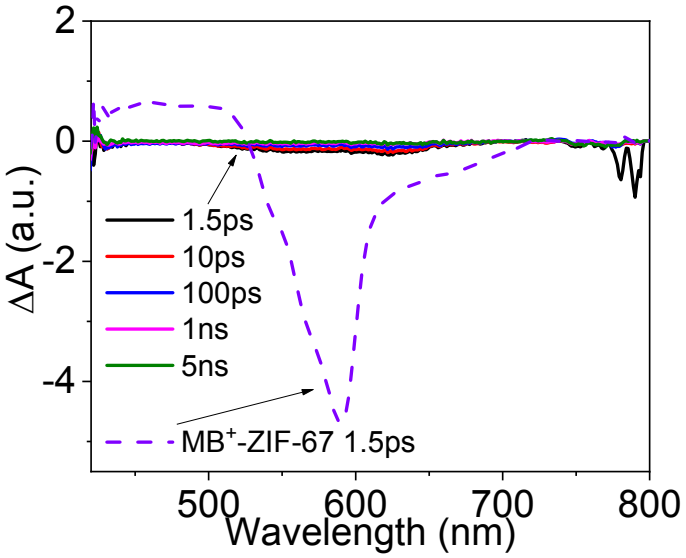

Figure S2. The transient absorption (TA) spectra of control MB^+-Quartz film following 1000nm excitation. The TA signal due to direct excitation of MB^+ in MB^+-Quartz film is negligible compared to the ground state bleach signal of MB^+ in MB^+-ZIF-67 collected under the same experimental conditions.

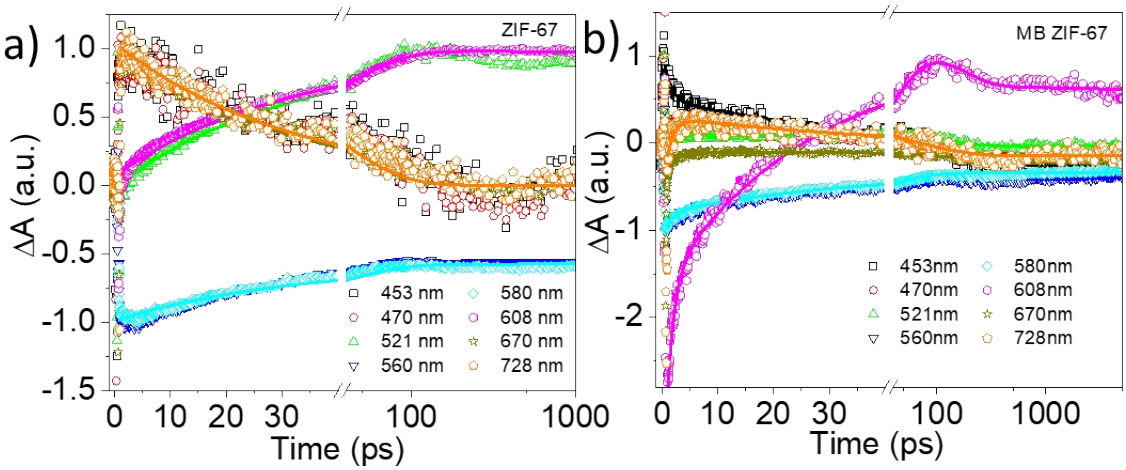

Figure S3. Full kinetic fitting data for ZIF-67 (a) and MB^+-ZIF-67 (b). Eight representative kinetic traces across the TA spectra were chosen and global fit using the same multiexponential model. Details are given in the supplementary fitting information following Table S1.

Table S1. Multiexponential fit results for eight representative wavelengths across the TA spectra. The time constants associated with each numbered amplitude are: 31.7 ps, 1.33 ps, 101.4 ps, and >>5ns, for A1-4 respectively. Superscript A^r denotes the amplitude as a rising component. In MB+-ZIF-67, for 560nm, 580nm, 608nm, 670nm, and 728 nm, rising component is defined as opposite in sign from A_4 component. For 453 nm, 470 nm, and 521 nm, the rising component for A_4 represents the slightly negative feature at >>5ns due to MB^+ GSB.

Sample	Amp.	453nm	470nm	521nm	560nm	580nm	608nm	670nm	728nm
ZIF-67	A1	100	100	50.3^r	46.2	41.6	48.2^r	100	100
	A2	-	-	-	-	-	-	-	-
	A3	-	-	-	-	-	-	-	-
	A4	0	0	49.7	53.8	58.4	51.8	0	0
MB+ ZIF-67	A1	20.2	18.4	27.8^r	39.7	41.9	42.1^r	4.7	12.7^r
	A2	36.8	35.1	10.6	21.6	26.4	36.0^r	60.0	61.1
	A3	26.9	28.0	52.8	5.9^r	1.3^r	14.0	14.9^r	16.5^r
	A4	16.1^r	18.5^r	8.8^r	32.8	30.3	7.9	20.4	9.7

Multiexponential fitting model

The multiexponential fitting model chosen is a sum of four exponential decay functions. The initial model for ZIF-67 is informed by our previous work on ZIF-67 photodynamics[1] and only consists of two exponentials (31.7ps and >>5ns). As is evident in Figure S3a, only a single exponential decay is present at the broad positive features at 453 nm, 470 nm, 670 nm, and 728nm through the 31.7ps time constant. These traces are all overlaid in Figure S3a. The other, more intense positive features at 521nm and 608nm grow with very similar kinetics during the 31.7ps event that we have previously assigned to formation of charge-separated state with LMCT character. Lastly, the wavelengths associated with GSB of Co d-d transition (560 and 580 nm) decay during the 31.7ps event. The >>5ns component accounts for remaining signal after our available time window.

For MB^+-ZIF-67, there are two time regions of spectral evolution that can be observed from the TA spectra, i.e some event at very early times (notably fast GSB decay that greatly exceeds 31.7ps) and some event on the order of 100ps (observable as growth at 670nm). As such, two additional time components were included in the fit. The global best fit for these components across all 8 wavelengths fitted is 1.33ps and 101.4ps, which are assigned in detail in the main text.

1) Pattengale, B.; Yang, S.; Ludwig, J.; Huang, Z.; Zhang, X.; Huang, J. *J. Am. Chem. Soc.* **2016**, *138*, 8072.