ADVANCED FUNCTIONAL MATERIALS

# Supporting Information

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## Antibacterial Films Based on MOF Composites that Release Iodine Passively or Upon Triggering by Near-Infrared Light

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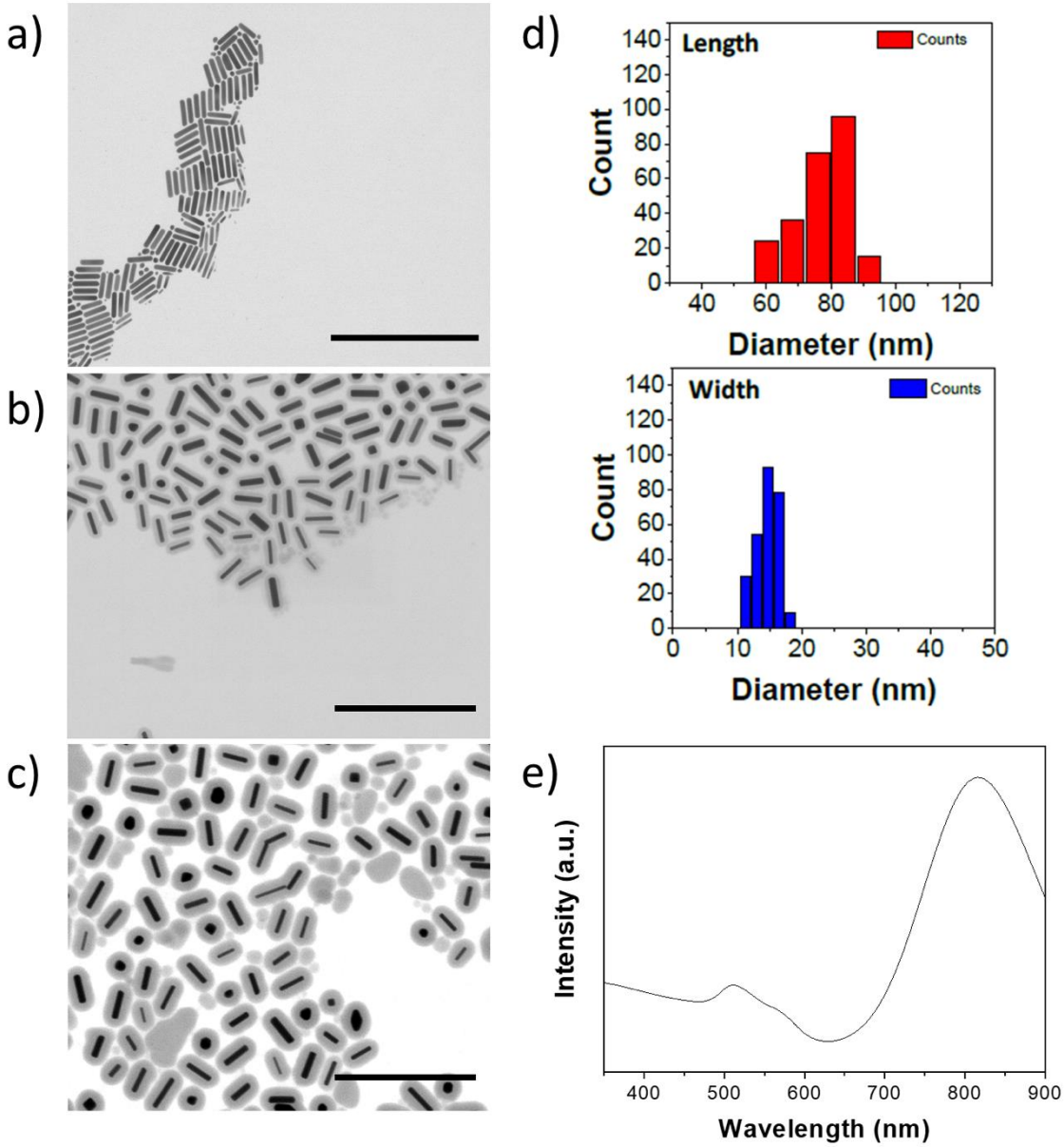


**Figure S1.** (a) Bright field STEM image of the synthesized AuNRs. (b) Bright field STEM image of the AuNR@$SiO_2$ after the first silica-shell coating. The shell size obtained after the coating was 17.5 ± 1.96 nm (c) Bright field STEM image of the AuNR@$SiO_2$ after the second silica-shell coating. The shell size obtained after the second coating was 30 nm ± 3 nm. (d) Length 77.5 ± 8.06 nm and width 14.6 ± 1.73 nm calculated size distribution of the synthesized AuNRs. The NPs presented an aspect ratio of: 5.00. (e) UV-Vis spectra of the synthesized AuNRs NPs, showing the LSRP peak maximum at 810 nm.

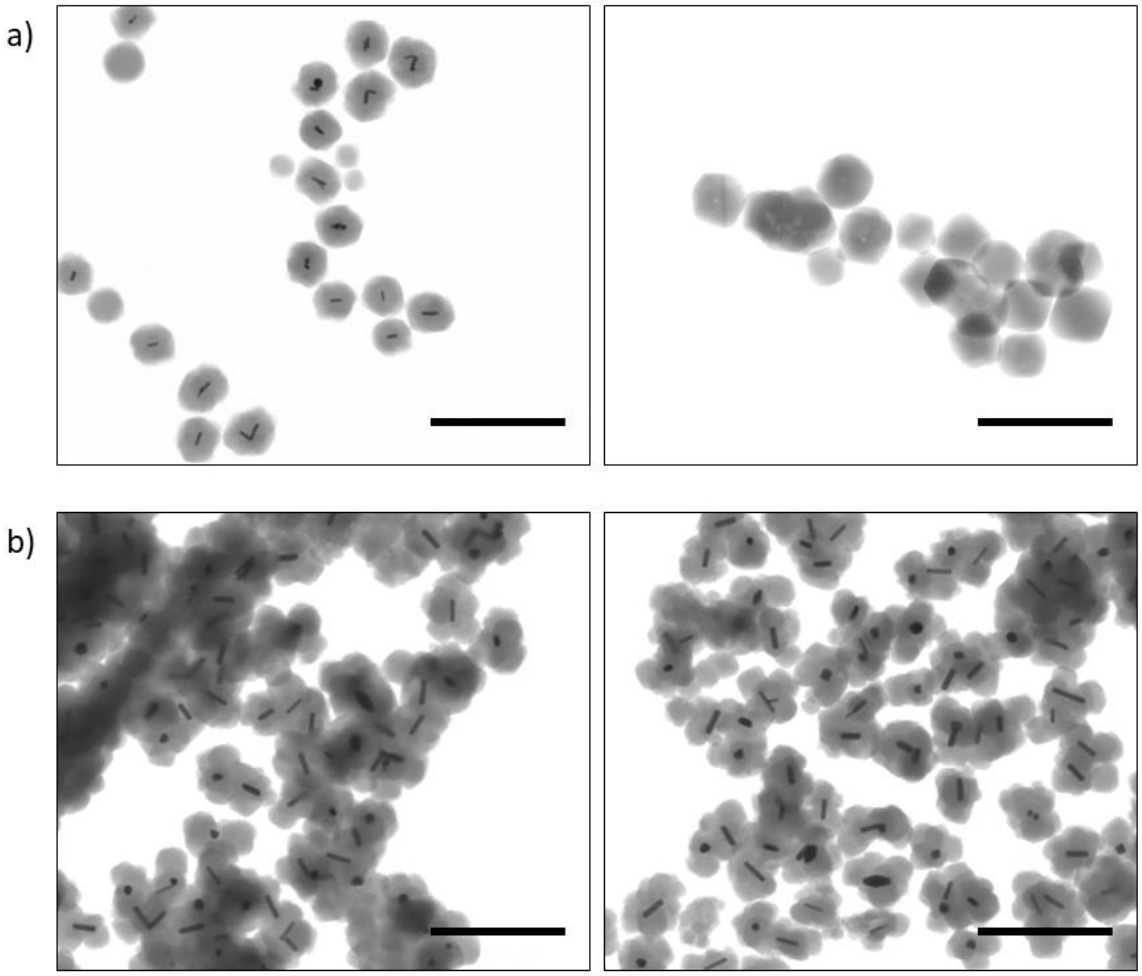


**Figure S2.** (a) STEM micrographs of synthesized AuNR@UiO-66 composite before (left) and after (right) exposure to iodine gas at 75 °C for 3 hours. Note that the AuNRs were etched after having been exposed to the iodine. (b) STEM micrographs of the AuNR@$SiO_2$@UiO-66 composite before (left) and after (right) exposure to iodine at 75 °C for 96 hours, confirming the stability of the silica-coated AuNRs. Scale bar: 500 nm.

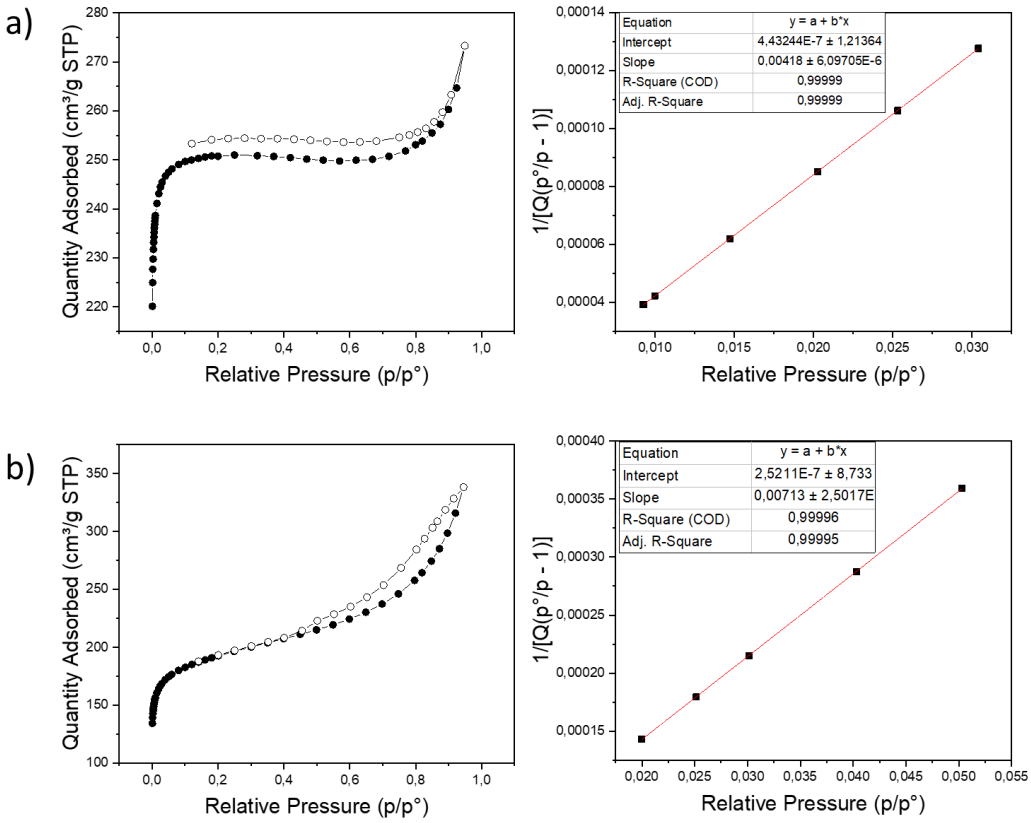


**Figure S3.** $N_2$-sorption isotherm measurements at 77 K, and corresponding BET plots, for UiO-66 microbeads (a) and AuNR@$SiO_2$@UiO-66 microbeads (b).

| Material | Temperature (°C) | | |
|---|---|---|---|
| | 1000 mW $cm^{-2}$ | 224 mW $cm^{-2}$ | 52 mW $cm^{-2}$ |
| UiO-66 | 25 | 24 | 24 |
| AuNR@$SiO_2$@UiO-66 | 274 | 150 | 90 |
| UiO-66 after desorption | 48 | 32 | 26 |
| AuNR@$SiO_2$@UiO-66 after desorption | 269 | 145 | 86 |

**Table S1.** Summary of the maximum temperatures reached by each studied material upon irradiation with near-infrared lasers of different intensities.

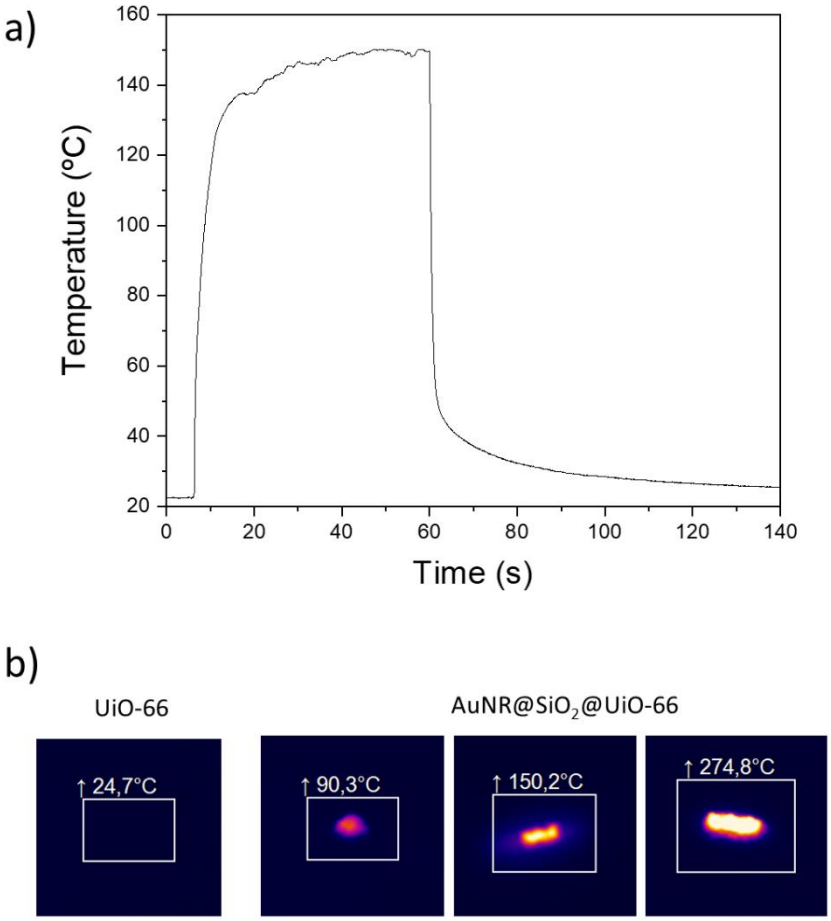


**Figure S4.** (a) Plot of time vs. temperature for AuNR@$SiO_2$@UiO-66 microbeads irradiated for 1 minute with near infrared light at an intensity of 224 mW $cm^{-2}$. (b) Thermal imaging of the UiO-66 (leftmost) when irradiated at 1000 mW $cm^{-2}$, and AuNR@$SiO_2$@UiO-66 microbeads when irradiated with an intensity of 52 mW $cm^{-2}$ (left), 224 mW $cm^{-2}$ (middle) and 1000 mW $cm^{-2}$ (right).

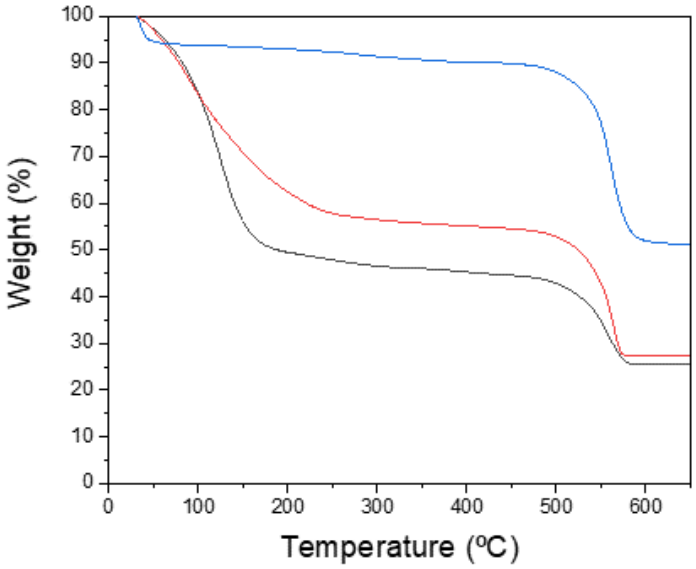


**Figure S5.** Thermogravimetric analysis curves for pristine UiO-66 microbeads (blue), iodine-loaded UiO-66 microbeads (black), and iodine-loaded AuNR@$SiO_2$@UiO-66 microbeads (red).

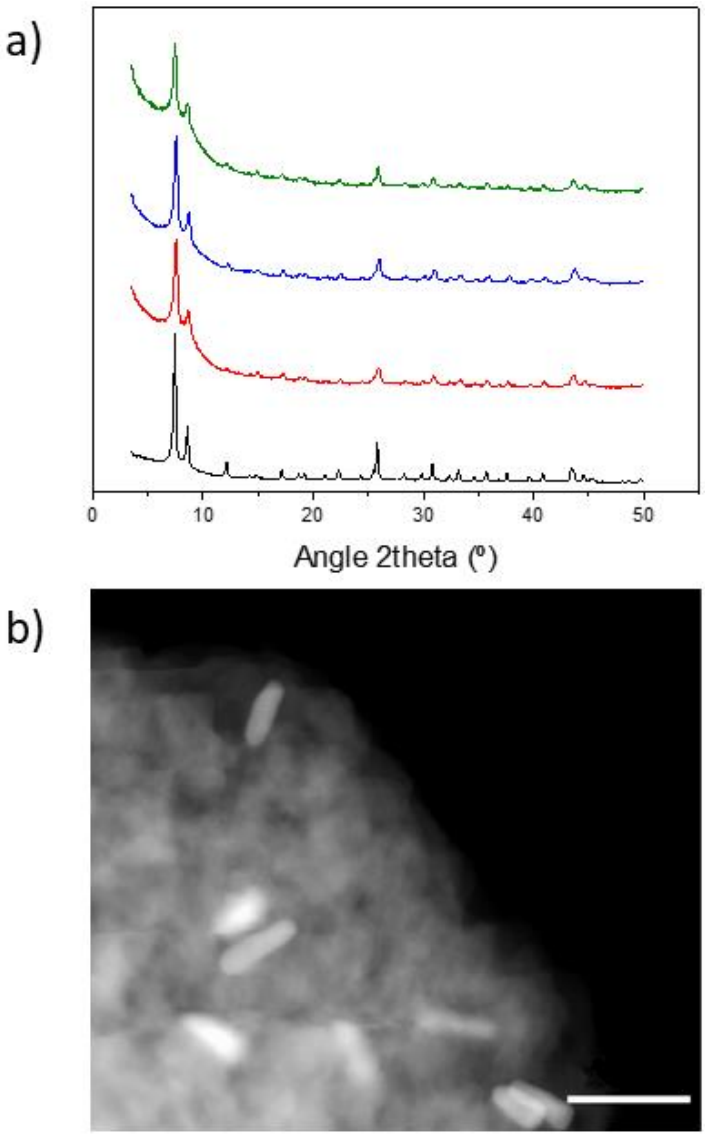


**Figure S6.** (a) PXRD spectra of pristine UiO-66 (black), pristine AuNR@$SiO_2$@UiO-66 (red), UiO-66 after desorption of iodine (blue), and AuNR@$SiO_2$@UiO-66 after desorption of iodine (green). (b) HAADF-STEM micrograph of AuNR@$SiO_2$@UiO-66 after 96-hour exposure to iodine at 75 °C. Scale bar: 100 nm.

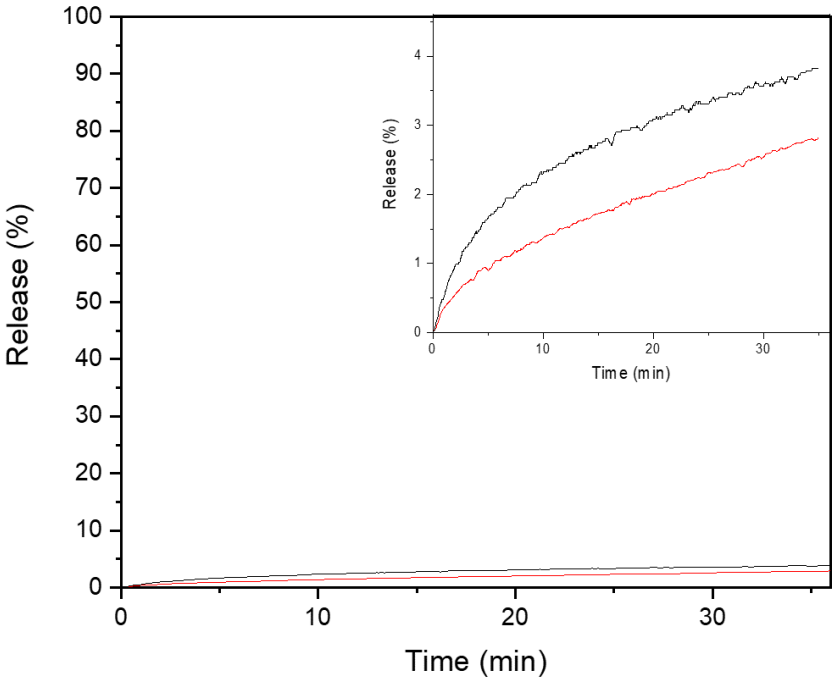


**Figure S7.** Release of iodine from $I_2$@UiO-66 microbeads (black) and $I_2$@AuNR@$SiO_2$@UiO-66 microbeads (red), without any laser irradiation. Inset: zoomed section of graph.

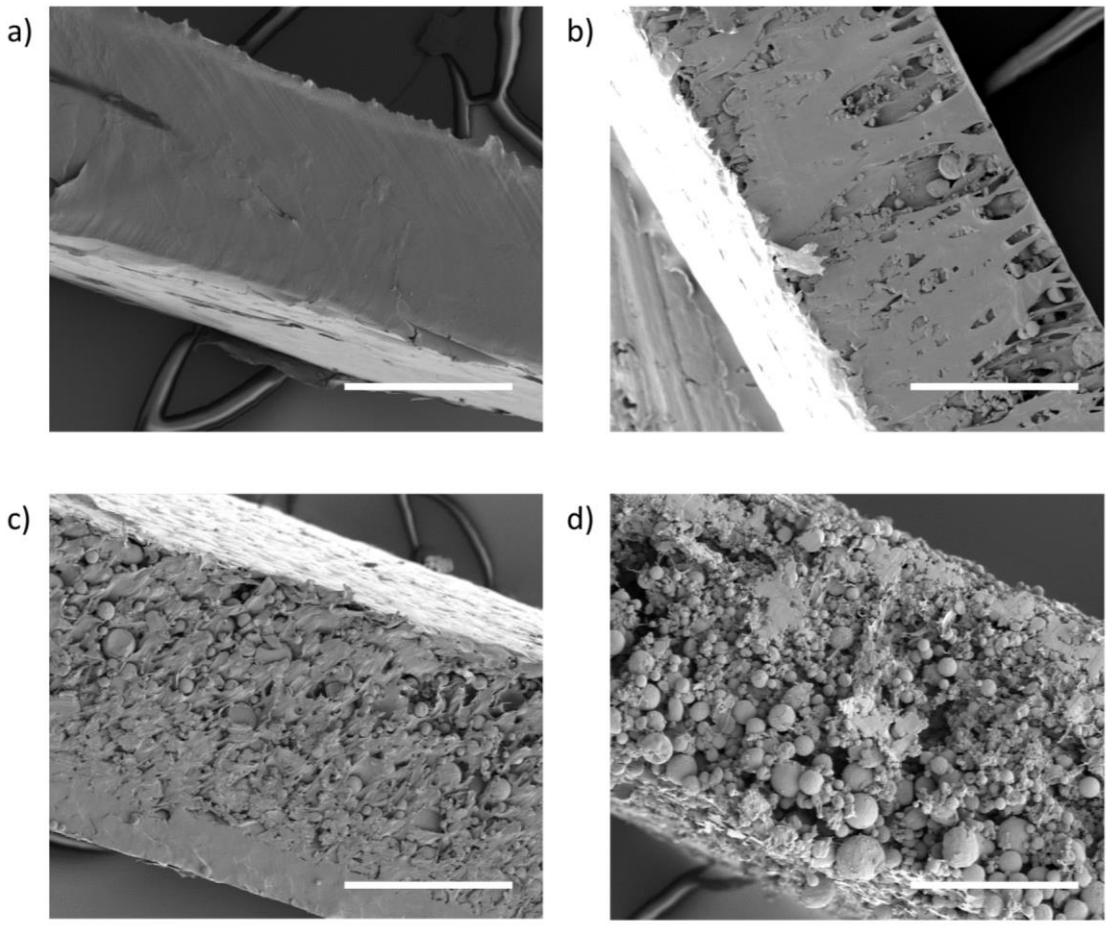


**Figure S8.** FE-SEM micrographs of cross-sections of the composite films containing AuNR@$SiO_2$@UiO-66 microbeads at 0% (a), 8% (b), 25% (c) and 46 (d)% (w/w).

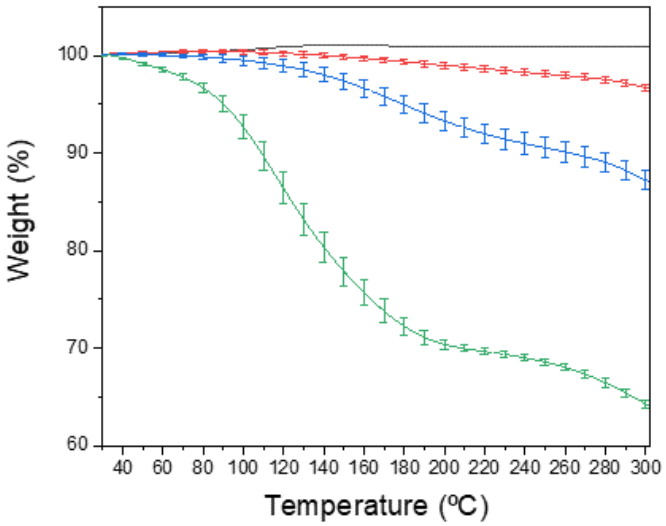


**Figure S9.** TGA curves of the iodine-loaded composite films containing AuNR@$SiO_2$@UiO-66 microbeads at 0% (black), 8% (red), 25% (blue) and 46% (green) (w/w).

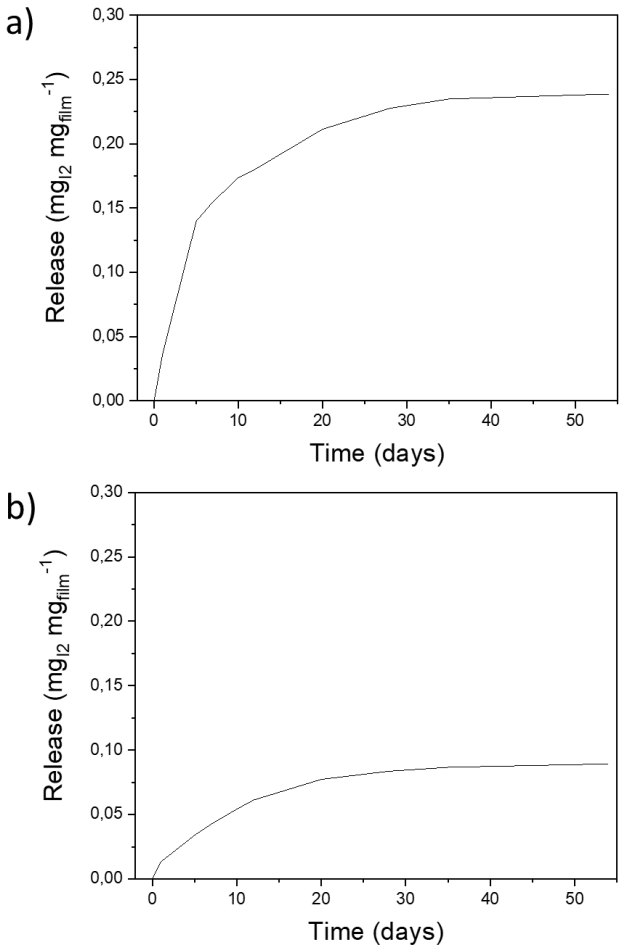


**Figure S10.** Iodine release over time from the composite films containing AuNR@$SiO_2$@UiO-66 microbeads at 46% (a) and 25% (b) (w/w), without any laser irradiation.

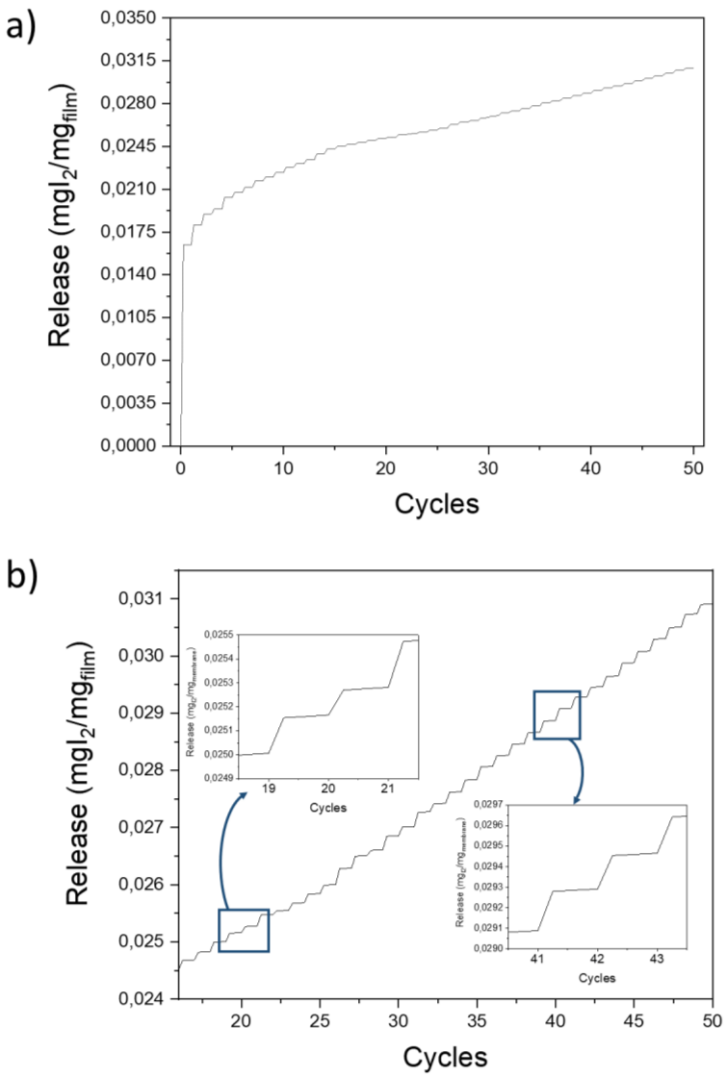


**Figure S11** (a) Stepwise release of iodine from a composite film containing $I_2$@AuNR@$SiO_2$@UiO-66 microbeads at 25% (w/w) irradiated with NIR light at 224 mW $cm^{-2}$ and subjected to on/off switching. (b) Zoom on the stepwise release after its stabilization at the fifteenth cycle.

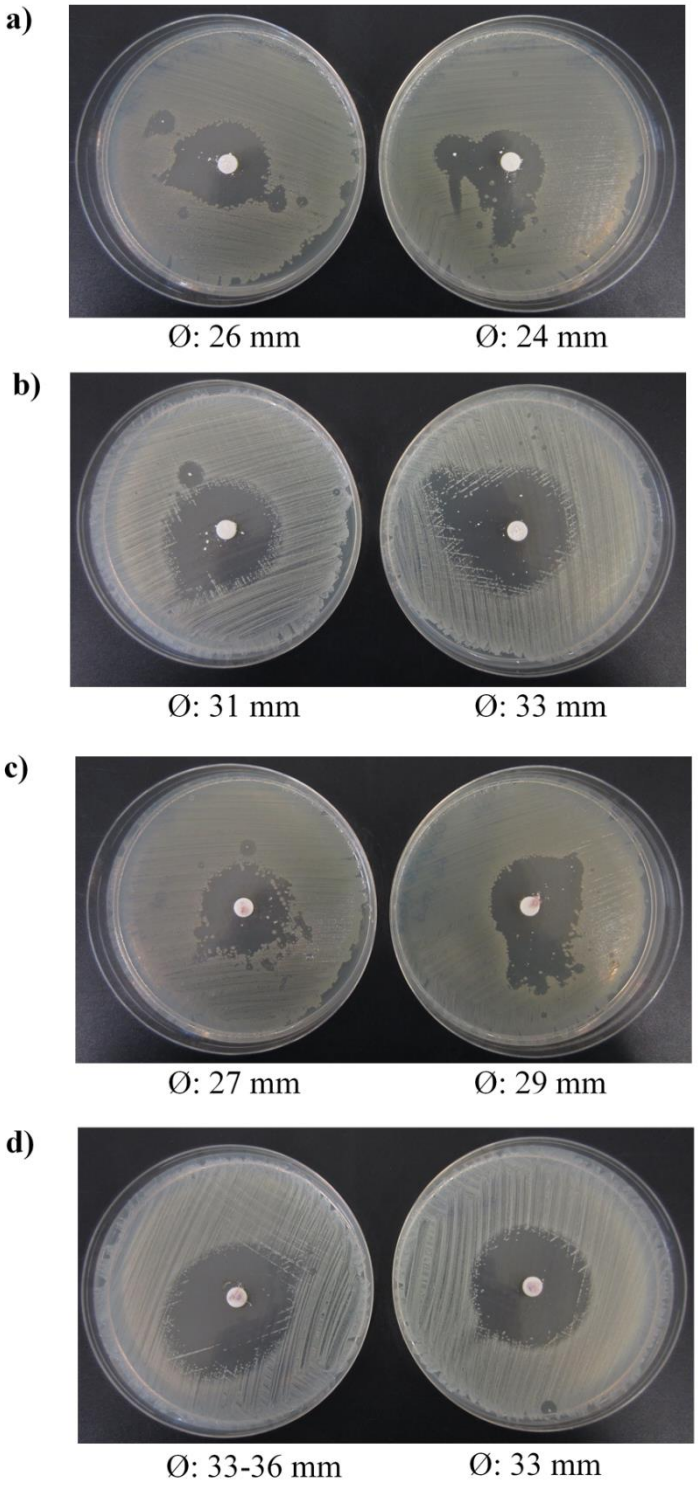


**Figure S12.** Growth-inhibition zones induced by $I_2$@UiO-66 microbeads (a, b) and $I_2$@AuNR@$SiO_2$@UiO-66 microbeads (c, d) against *E. coli* (a, c) or *S. aureus* (b, d) cultures, either after near-infrared light irradiation (left) or without irradiation (right). Ø: diameter of growth-inhibition zone. Disc diameter: 6 mm.

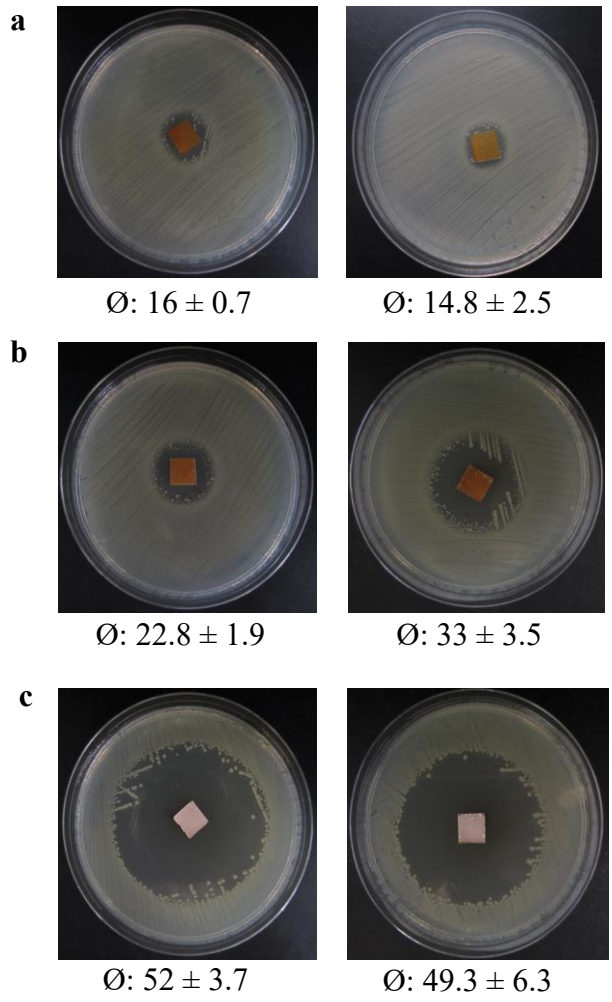


**Figure S13.** Growth-inhibition zones induced by square sections of composite films containing iodine-loaded AuNR@$SiO_2$@UiO-66 at 8% (a), 25% (b) and 46% (c) (w/w), against *E. coli* cultures, either after near-infrared light irradiation (left) or without irradiation (right). Ø: diameter of growth-inhibition zone. Film size: 1 $cm^2$. Values are the average of at least five replicates ± standard deviation.

**Table S2.** Growth-inhibition of composite films prepared at different iodine-containing microbead-loadings (8%, 25% or 46%) and tested on *E. coli* cultures.

| Composite (%) | Ø non irradiated with NIR (mm)[a] | Ø irradiated with NIR (mm)[a] |
|---|---|---|
| AuNR@SiO2@UiO-66 (8%) | 14.8 ± 2.5 | 16 ± 0.7 |
| AuNR@SiO2@UiO-66 (25%) | 33 ± 3.5 [b] | 22.8 ± 1.9 |
| AuNR@SiO2@UiO-66 (46%) | 49.3 ± 6.3[b] | 52 ± 3.7 [c] |

[a] Each value is the average of at least five replicates ± standard deviation.
[b] Statistically significant differences between 25 and 46% compositions with respect to 8% within non irradiated group ($P < 0.0001$).
[c] Statistically significant differences between 46% composition with respect to 8 and 25% within irradiated group ($P < 0.0001$).

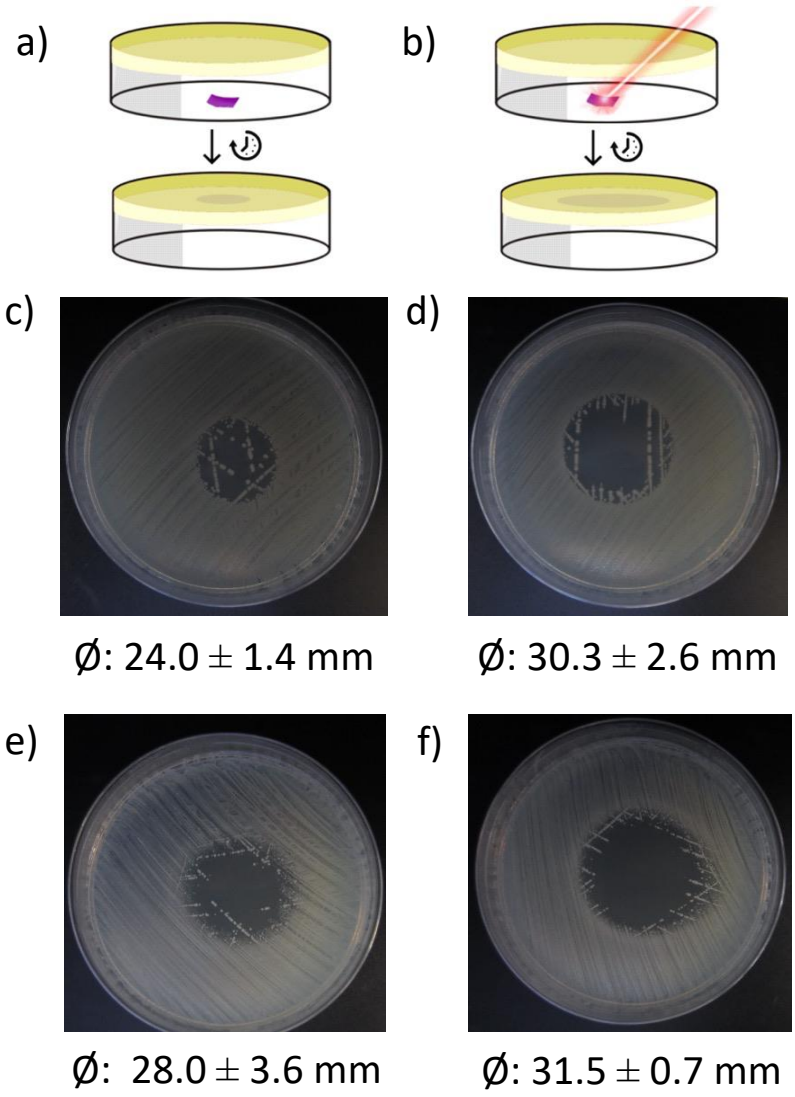


**Figure S14.** (a-b) Schematic illustrations of the two experiments performed to study the passive (a) or light-triggered (b) antibacterial performance of the films containing iodine-loaded UiO-66 microparticles. (c-f) Corresponding inhibition growth zones of *E. coli* (c-d) and *S. aureus* (e-f) cultures produced in composite films containing UiO-66 microparticles at 25% (w/w). Left and right: photographs taken after co-incubation of both film and agar plate inoculated with *E. coli* (c-d) and *S. aureus (e,f)* once the films had been removed. The films shown in (d,f) had been irradiated with NIR light. Ø: diameter of the growth-inhibition zone.

**Table S3.** Growth-inhibition diameters (Ø) in *E. coli* cultures created by composite films containing iodine-loaded AuNR@$SiO_2$@UiO-66 microbeads at 8% and 25%.

| Composite (%) | Ø non irradiated with NIR (mm), film removed[a] | Ø irradiated with NIR (mm), film removed[a] | Ø non irradiated with NIR (mm), film not removed[a] |
|---|---|---|---|
| AuNR@$SiO_2$@UiO-66 (8%) | 3.7 ± 4.3 | 15.6 ± 3.8 [b] | 12.5 ± 2.4 [c] |
| AuNR@$SiO_2$@UiO-66 (25%) | 27 ± 3.7 | 41.6 ± 2.7 [b] | 38 ± 5 [c] |

[a] Each value is the average of at least four replicates ± standard deviation.
[b] Statistically significant difference between non irradiated and irradiated with NIR film removed at 8% composite ($P = 0.0002$) and at 25% composite ($P < 0.0001$).
[c] Statistically significant difference between non irradiated with NIR film removed and not removed at 8% composite ($P = 0.0047$) and at 25% composite ($P = 0.0023$).

**Table S4.** Growth-inhibition diameters (Ø) in *S. aureus* cultures created by composite films containing iodine-loaded AuNR@$SiO_2$@UiO-66 microbeads at 8% and 25%.

| Composite (%) | Ø non irradiated with NIR (mm), film removed[a] | Ø irradiated with NIR (mm), film removed[a] | Ø non irradiated with NIR (mm), film not removed[a] |
|---|---|---|---|
| AuNR@$SiO_2$@UiO-66 (8%) | 14.6 ± 5.7 | 19.5 ± 1.3 | 20.8 ± 3.4 |
| AuNR@$SiO_2$@UiO-66 (25%) | 25.3 ± 5.4 | 43.2 ± 4.3 [b] | 45 ± 3.8 [b] |

[a] Each value is the average of at least four replicates ± standard deviation.
[b] Statistically significant differences between irradiated with NIR film removed and non-irradiated film not removed regarding non irradiated film removed ($P < 0.0001$).