

Electronic Supporting Information for:

Pesticide luminescent detection and degradation using NU-1000 MOF

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Table S1. Summary of NU-1000 particle lengths and widths observed by SEM

Synthesis of tetraethyl 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoate (1)

Tetrabromopyrene (5 g), 4-ethoxycarbonylphenylboronic acid (8.2 g), tripotassium phosphate (16.5 g) and tetrakis(triphenylphosphine)palladium(0) (0.75 g) were dissolved in degassed dioxane (270 mL). The reaction mixture was refluxed for 72 h at 90°C under argon, and the formation of a yellow precipitate was observed. Deionised water (200 mL) was then added and the mixture was cooled down. The precipitate was filtered through a Büchner funnel and washed with water (2 x 100 mL) and acetone (200 mL). The solid yellow residue was recovered, dissolved in 300 mL chloroform and reduced to 150 mL under vacuum. Methanol (300 mL) was then added and the yellow precipitate that formed was filtered through a Büchner funnel and dried under vacuum (6.36 g; yield, 83%).
 ^1H NMR (400 MHz, CDCl_3 , 25°C) δ (ppm): 8.23 (d, $^3J_{\text{HH}} = 8.82$ Hz, 8H, CH), 8.14 (s, 4H, CH), 8.00 (s, 2H, CH), 7.74 (d, $^3J_{\text{HH}} = 8.82$ Hz, 8H, CH), 4.45 (q, $^3J_{\text{HH}} = 7.1$ Hz, 8H, CH_2), 1.45 (t, $^3J_{\text{HH}} = 7.1$ Hz, 12H, CH_3).
 ^{13}C NMR (400 MHz, CDCl_3 , 25°C) δ (ppm): 166.66 (CO), 145.49 (C^{qt}), 136.81 (C^{qt}), 130.91 (CH), 129.97 (CH), 129.82 (C^{qt}), 129.39 (CH), 128.57 (C^{qt}), 125.97 (CH), 125.78 (C^{qt}), 61.29 (CH_2), 14.58 (CH_3).
FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}): 709.78 (w), 775.35 (w), 858.29 (w), 1022.23 (w), 1099.38 (s), 1176.53 (w), 1271.04 (s), 1365.55 (w), 1606.64 (m), 1716.58 (s), 2979.9 (w).

Synthesis of H_4TBAPy (4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid)

Tetraethyl 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoate (0.87 g) was dissolved in 95 mL of dioxane before adding 75 mL of a 0.3 M solution of potassium hydroxide. The reaction mixture was refluxed for 40 h at 120°C before being left to cool. A concentrated solution of hydrogen chloride (37%) was then slowly added through a dropping funnel under stirring until the reaction reached a pH of 1. A yellow precipitate formed and the reaction mixture was stirred for 1 h. The precipitate was filtered, suspended in 20 mL of water and sonicated for 1 h. The solid residue was then filtered, washed with water (20 mL), dried under vacuum for 4 h, dissolved once more in 20 mL of boiling DMF (140–150°C), filtered while hot through a cannula, and the filtrate was left to dry. Dichloromethane (60 mL) was added and stirred for 30 min to precipitate H_4TBAPy . The solid residue was filtered, washed with dichloromethane (20 mL), dried under vacuum at 120°C for 18 h and ground (0.52 g; yield, 69%).
 ^1H NMR (400 MHz, DMSO, 25°C) δ (ppm): 8.22 (s, 4H, CH), 8.17 (d, $^3J_{\text{HH}} = 8.82$ Hz, 8H, CH), 8.09 (s, 2H, CH), 7.87 (d, $^3J_{\text{HH}} = 8.82$ Hz, 8H, CH).
 ^{13}C NMR (400 MHz, DMSO, 25°C) δ (ppm): 167.08 (CO), 144.05 (C^{qt}), 136.12 (C^{qt}), 130.64 (CH), 129.90 (C^{qt}), 129.53 (CH), 129.2 (CH), 127.45 (C^{qt}), 125.32 (CH), 125.06 (C^{qt}).
J-modulated NMR (400 MHz, DMSO, 25°C, Fig. S1) δ (ppm): 167.28 (CO), 144.24 (C^{qt}), 136.37 (C^{qt}), 130.84 (CH), 130.06 (C^{qt}), 129.70 (CH), 129.44 (CH), 127.66 (C^{qt}), 125.53 (CH), 125.27 (C^{qt}).
FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}): 709.78 (w), 777.28 (w), 860.22 (w), 1105.17 (w), 1178.46 (w), 1274.90 (m), 1417.62 (m), 1606.64 (s), 1693.43 (s), 2545.94 (w), 2650.09 (w), 2978-3067 (m, b), 3442.8 (m, b).

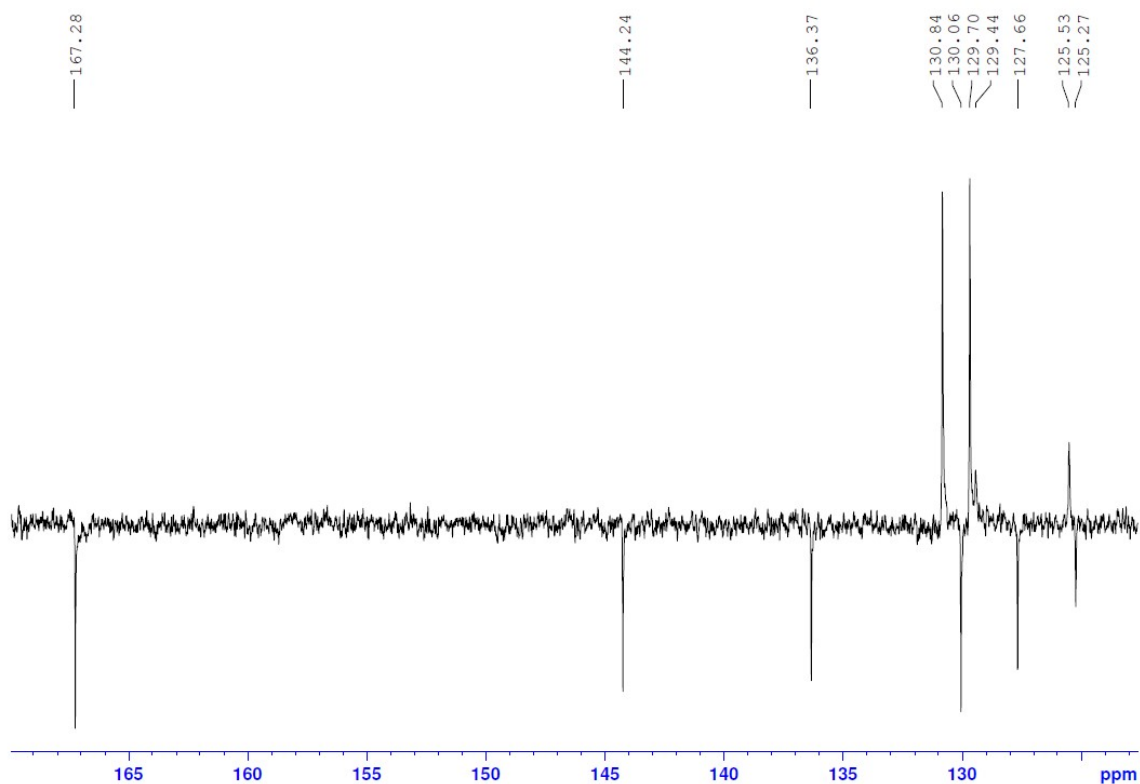


Fig. S1. J-modulated ¹H NMR spectrum of H₄TBAPy.

Synthesis of NU-1000

ZrOCl₂·8H₂O (388 mg) and benzoic acid (10.83 g) were ultrasonically dissolved in 32 mL of N,N-diethylformamide (DMF) in a 100 mL Pyrex tube and the solution was heated at 80°C in an oven for 1 h. After cooling down to room temperature, H₄TBAPy (166 mg) was added and the mixture was sonicated for 20 min and then heated at 100°C in an oven for 18 h. A yellow precipitate formed. After cooling down, the suspension was centrifuged (50-mL capped tube for 5 min, 1000 rpm at room temperature) and washed with DMF (3 x 45 mL). The resulting solid was transferred into a 100 mL Pyrex tube, dissolved in 52 mL of DMF and 2 mL of 8 M aqueous HCl was added. The suspension was heated at 100°C in an oven for 18 h. The suspension was then cooled down, centrifuged (5 min, 1000 rpm at room temperature), the supernatant was discarded and the resulting MOF was soaked in fresh DMF (45 mL) for 4 h. The MOF was then washed with (2 x 45 mL) and acetone (3 x 45 mL) under centrifugation (5 min, 1000 rpm at room temperature), with 12 h soaking between each acetone wash. The product was dried under vacuum and heated (209 mg; 38% yield). NU-1000 can be stored in a glovebox for several months. FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) : 470.61 (m), 642.27 and 657.70 (m), 715.56 (w), 785.00 (w), 864.07 (w), 1006.8 and 1018.37 (w), 1105.17 (w), 1180.39 (w), 1265 (w), 1413.77 (s),

1542.99 (m), 1604.71 (s), 1701.15 (w), 3421.6 (s, b). UV/Vis (NEM pH10 0.15 M, Fig. S2): $\lambda_{\max} (\epsilon) = 266$ nm (12405).

NU-1000 crystallographic data

The crystallographic data for NU-1000 were deposited in the Cambridge Crystallographic Data Centre (CCDC; deposition number 1580411). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. Vesta calculation parameters: $a = b \sim 40 \text{ \AA}$, $c \sim 17 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, consistent with a csq topology and P6/mmm space group.

Table S1. Summary of NU-1000 particle lengths and widths observed by SEM

	Length (μm)	Width (μm)
1	7.99	1.66
2	7.78	1.79
3	6.43	1.49
4	7.05	1.55
5	7.97	1.66
6	7.06	1.75
7	7.94	1.99
8	7.26	1.22
9	6.30	1.34
10	6.35	1.72
11	8.22	2.02
12	5.96	2.01
13	7.79	2.27
Min	5.96	1.22
Max	8.22	2.27
Mean	7.24	1.73
StdDev	0.77	0.29

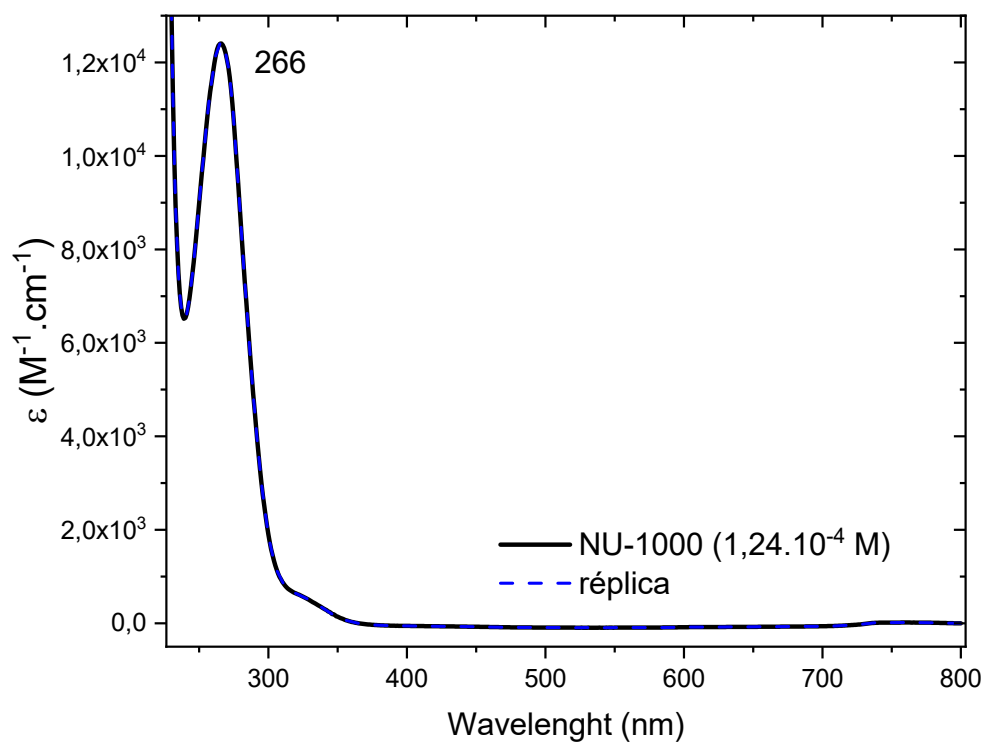


Fig. S2. UV-Vis spectrum of NU-1000

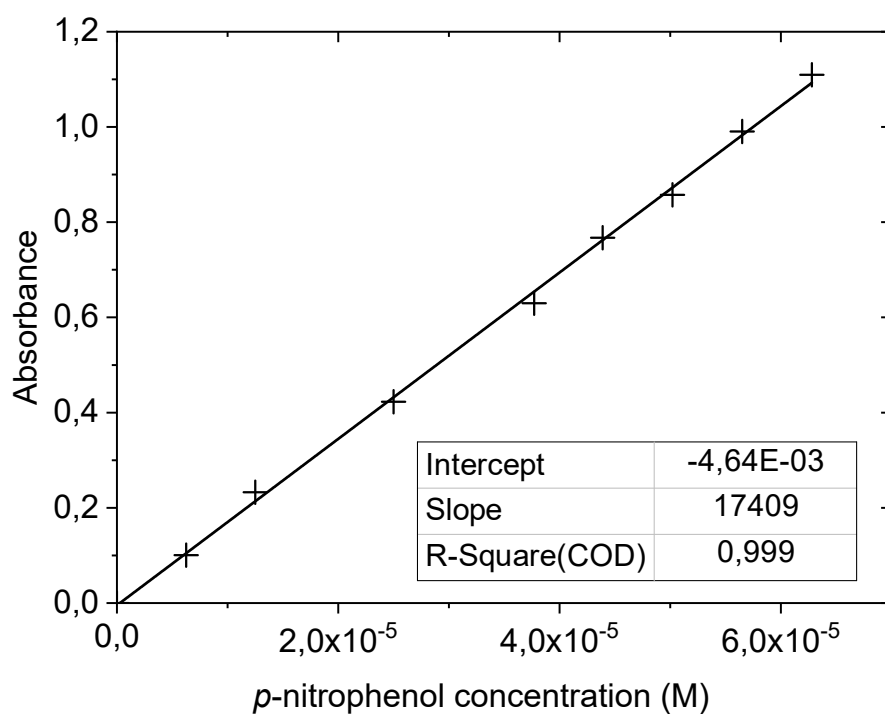


Fig. S3. *p*-nitrophenol absorbance vs concentration in NEM buffer over the range used in the hydrolysis experiments.

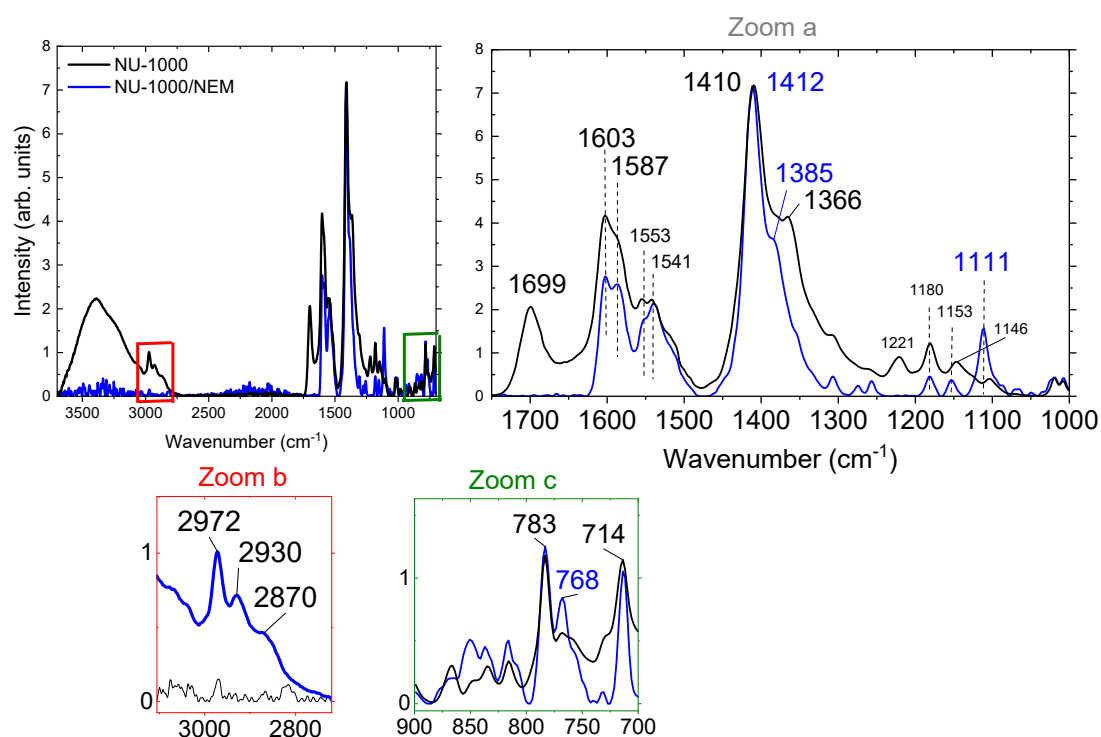


Fig. S4. ATR-FTIR spectra of NU-1000 and NU-1000/NEM. The band at 1699 cm^{-1} in the NU-1000 spectra is due to acetone contamination of the sample.

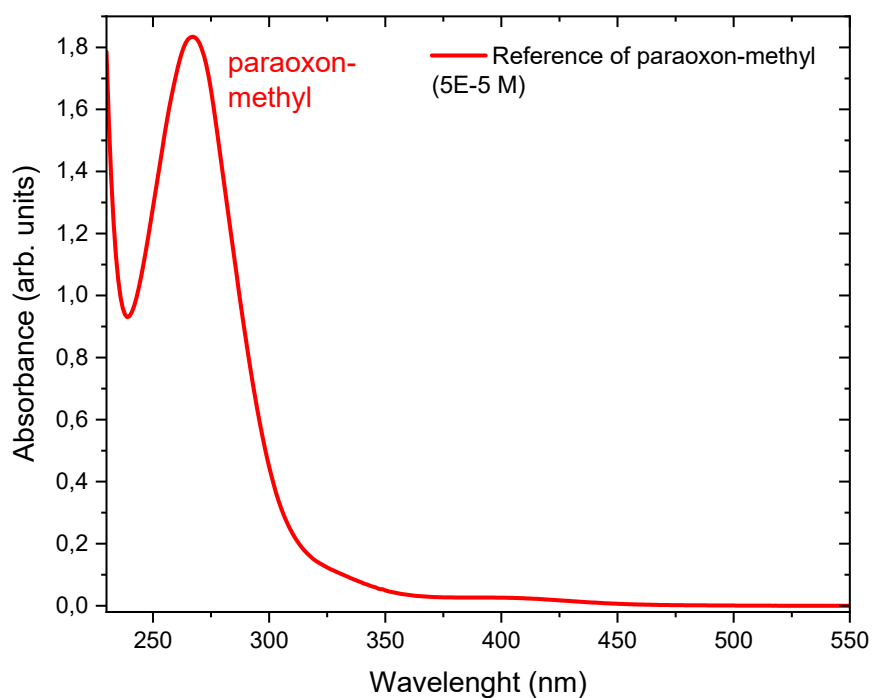


Fig. S5. Reference UV-Vis spectrum of methyl-paraoxon (DMNP) under standard conditions.

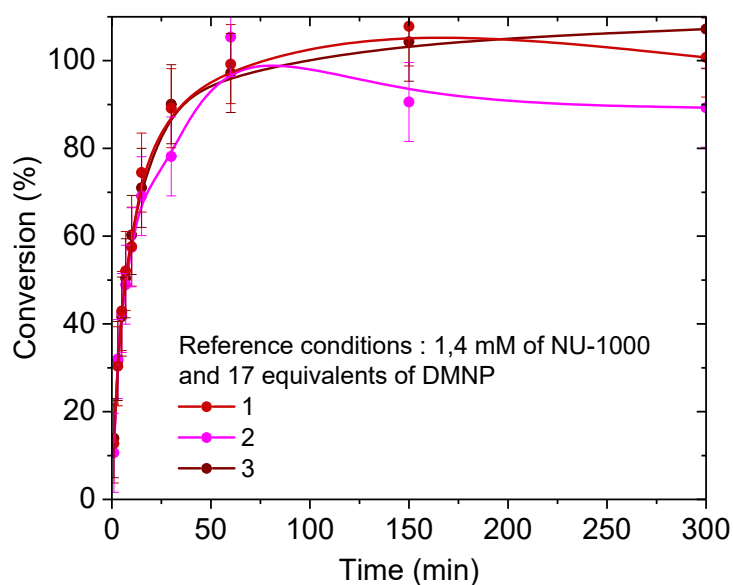


Fig. S6 Methyl-paraoxon conversion percentage (Eq. 1 in the main text) by NU-1000 as a function of time under reference catalysed hydrolysis conditions (methyl-paraoxon, $22 \text{ mmol}\cdot\text{L}^{-1}$; NU-1000, $1.4 \text{ mmol}\cdot\text{L}^{-1}$).

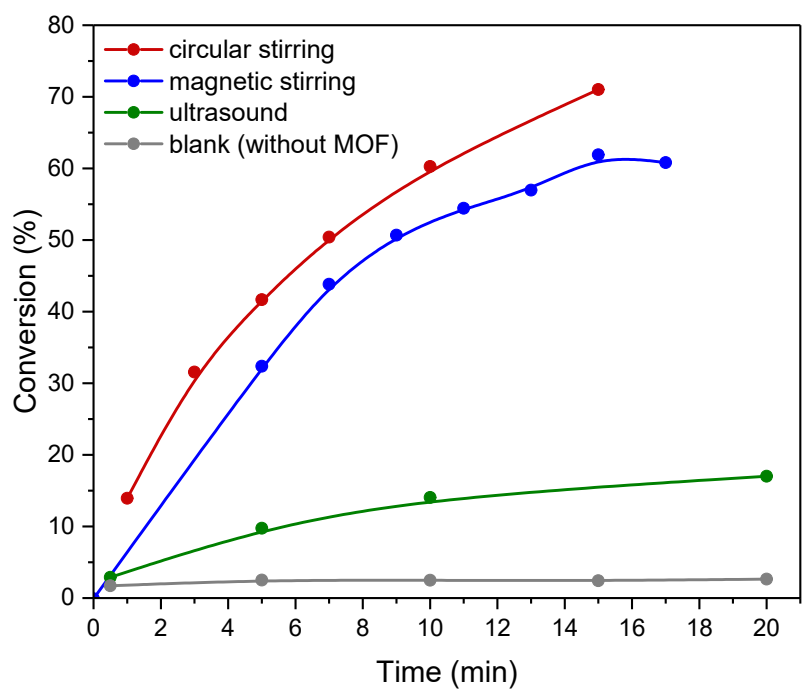


Fig. S7. Methyl paraoxon conversion percentage (Eq. 1 in the main text) by NU-1000 under different stirring conditions.

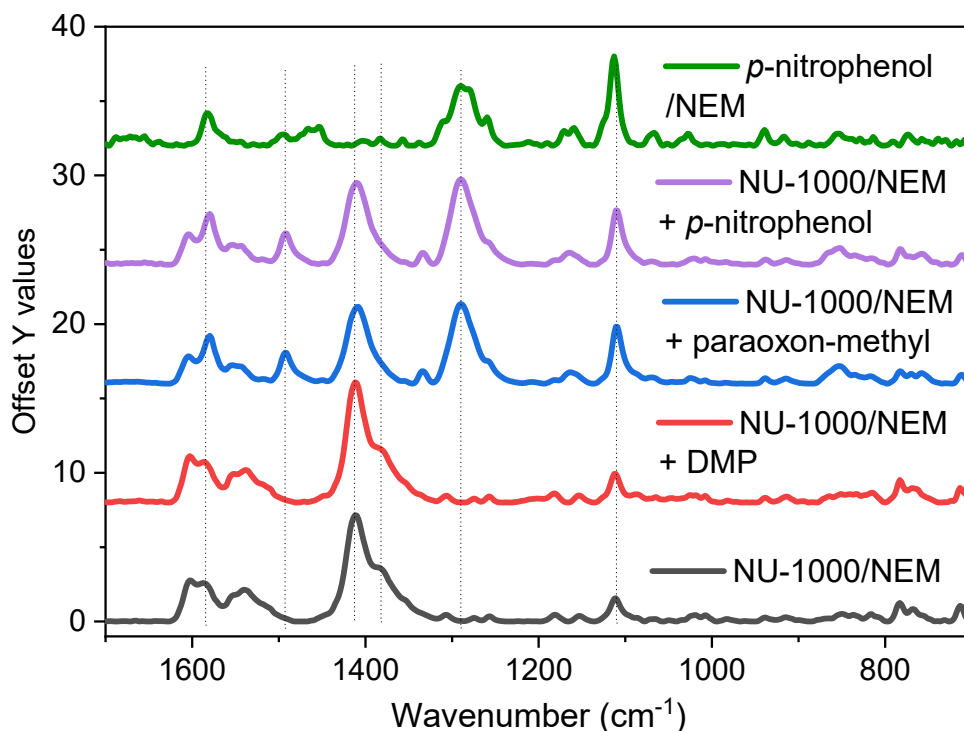


Fig. S8 ATR-FTIR spectra of NU-1000/NEM in isolation (black line) or in the presence of DMP (red), paraoxon-methyl (blue) and *p*-nitrophenol (purple), along with a reference spectrum of *p*-nitrophenol/NEM (green). The analytes were added at a 17-fold equivalent following the standard protocol (Table 1, line 2).

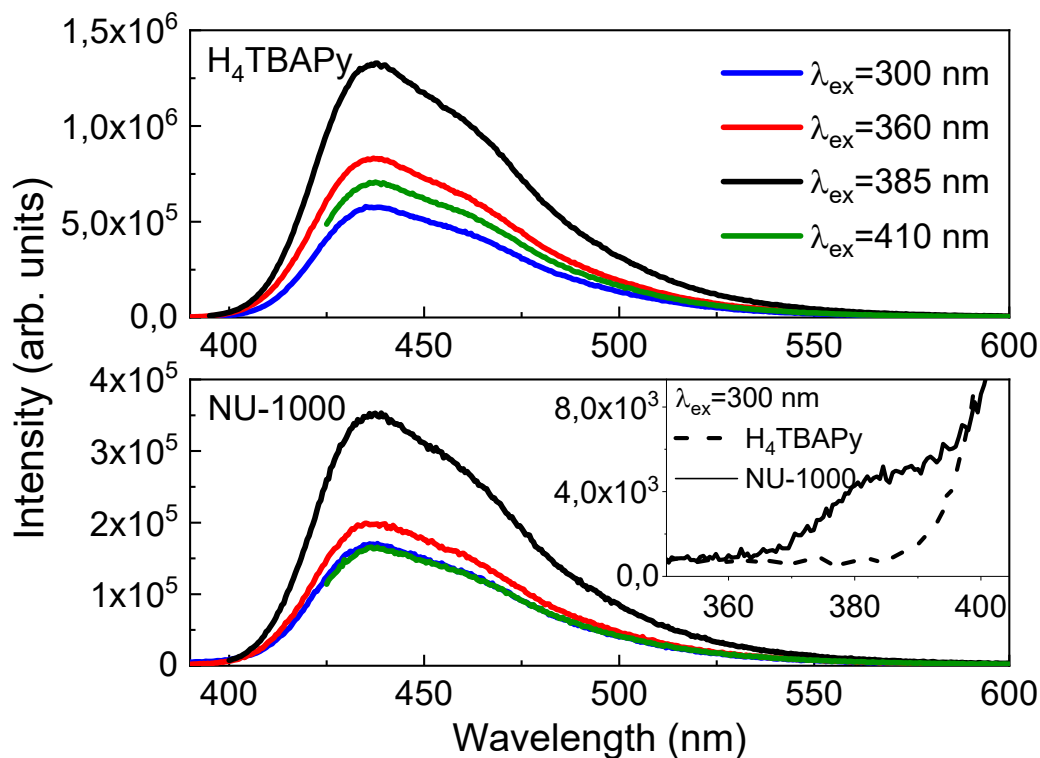


Fig. S9 Luminescence spectra of NU-1000 (bottom) and H_4TBAPy (top) at different excitation wavelengths.

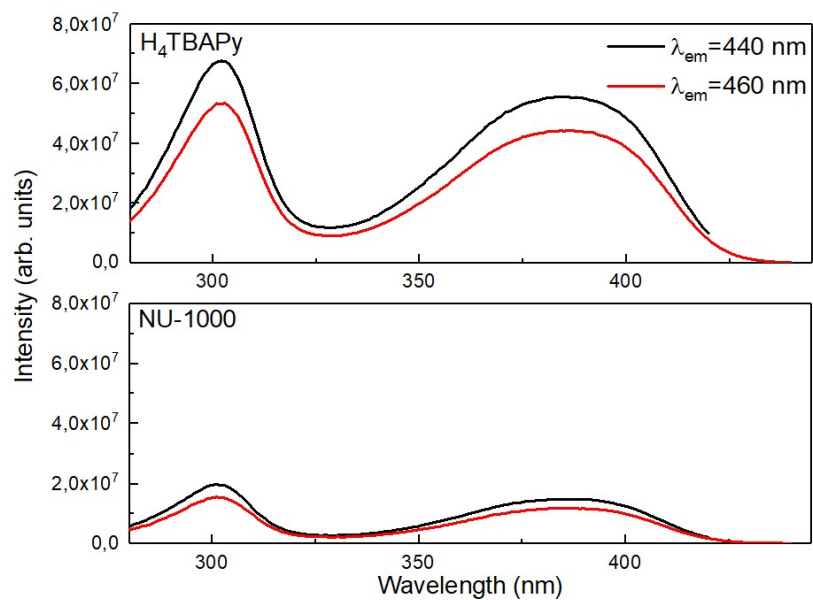


Fig. S10. Excitation spectra of H₄-TBAPy and NU-1000.

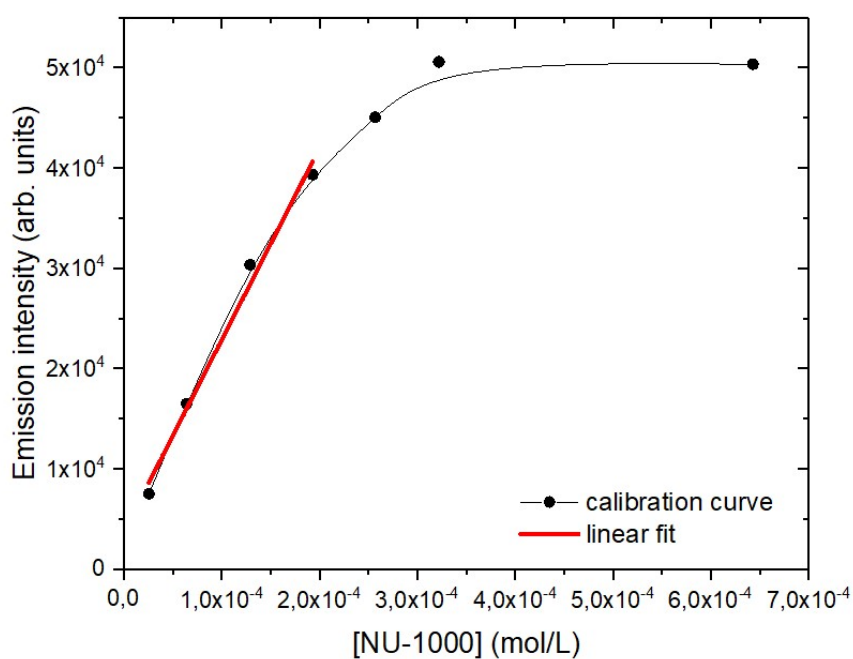


Fig. S11. Calibration curve and linearity range for the NU-1000.

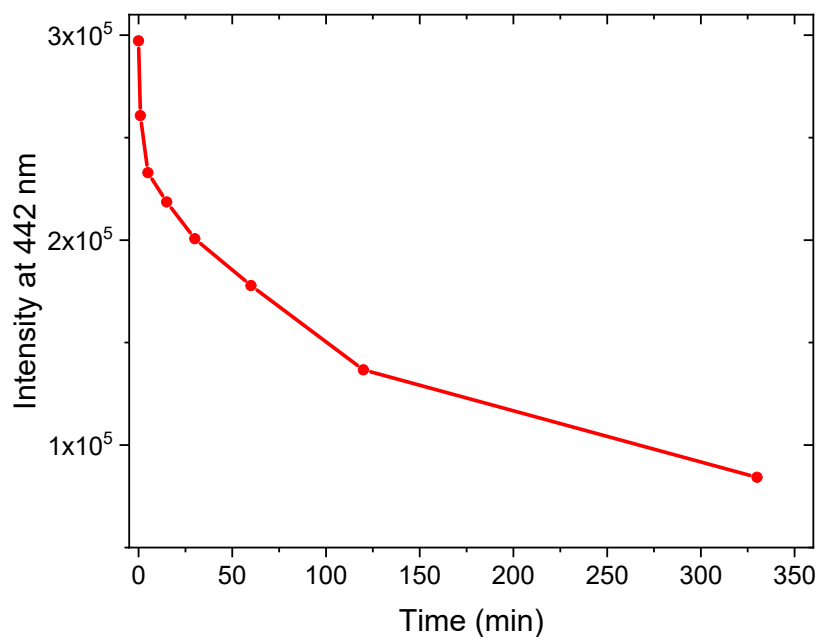


Fig. S12 Emission intensity at $\lambda = 442 \text{ nm}$ at different times during the degradation of paraoxon-methyl (1 mL of 0.09 mM NU-1000, 4 μL of paraoxon-methyl, 500 \times dilution prior to analysis).

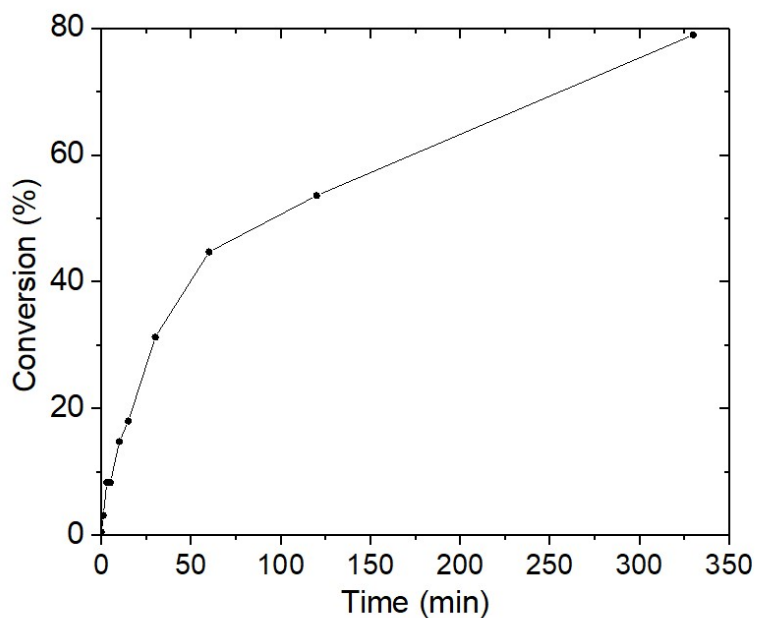


Fig. S13 Methyl-paraoxon conversion percentage (Eq. 1 in the main text) by NU-1000 as a function of time at low concentration (methyl-paraoxon, 22 $\text{mmol}\cdot\text{L}^{-1}$; NU-1000, 0.09 $\text{mmol}\cdot\text{L}^{-1}$).

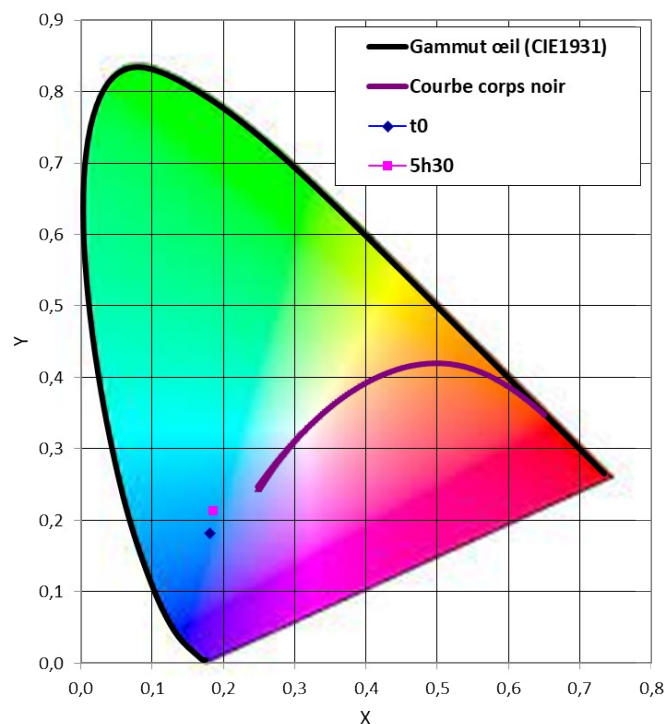


Fig. S14. Chromaticity diagram of NU-1000 CIE colorspace (xyz) evolution during the methyl paraoxon degradation by 0.09 mmol NU-1000.

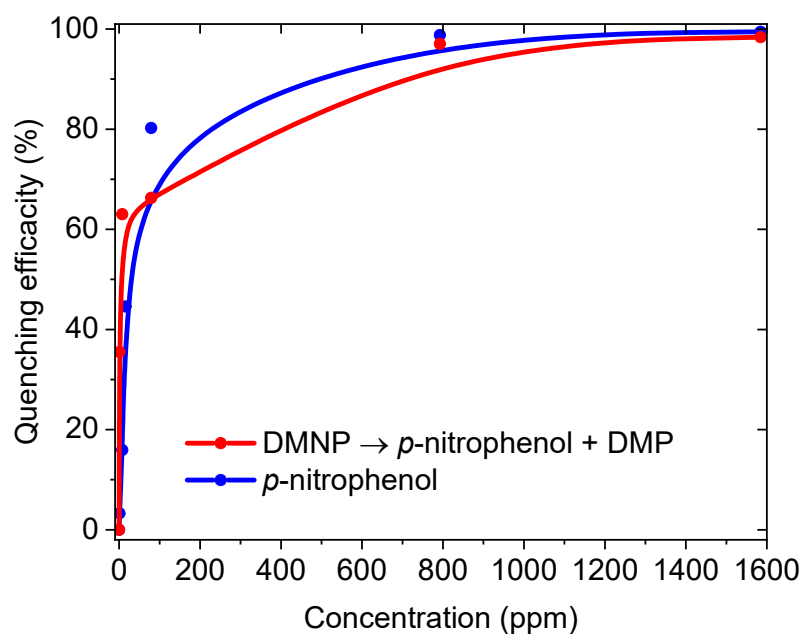


Fig. S15. NU-1000 emission in the presence of DMNP and p-nitrophenol at different concentrations following the automated measurement protocol with 0.05 mM of NU-1000 (1600 ppm = 10 molar eq.)

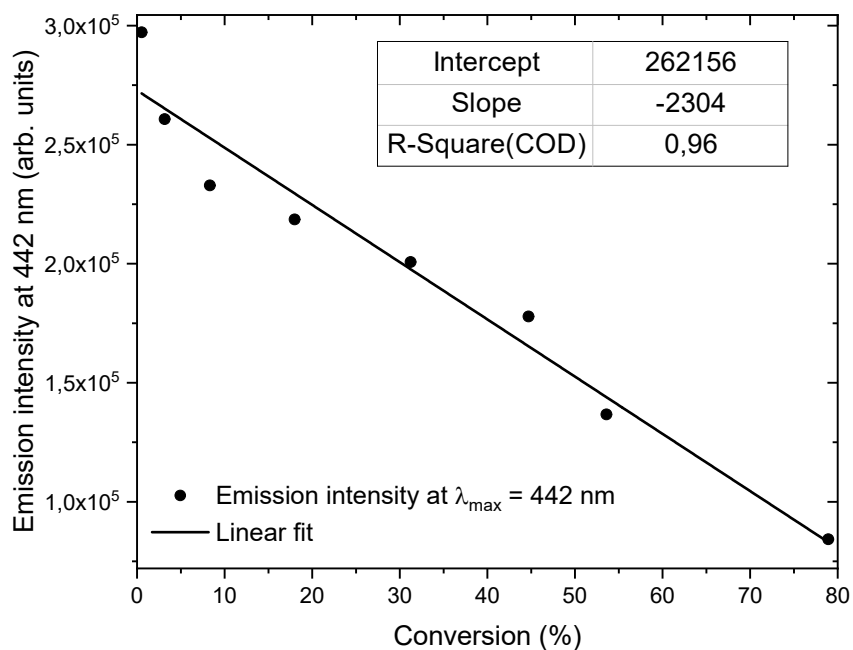


Fig. S16. Linear fit of the relationship between the NU-1000 emission intensity at 442 nm and the methyl paraoxon conversion percentage (Eq. 1 in the main text).

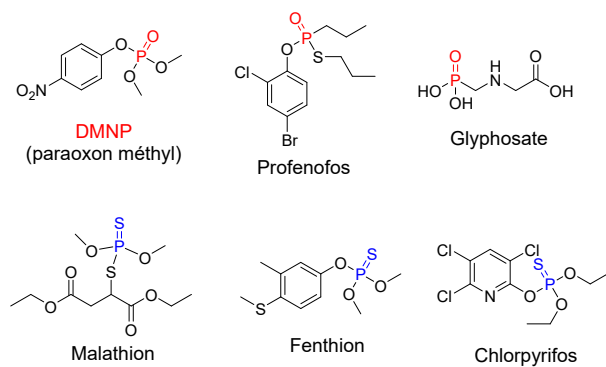


Fig. S17 Pesticides used in selectivity study

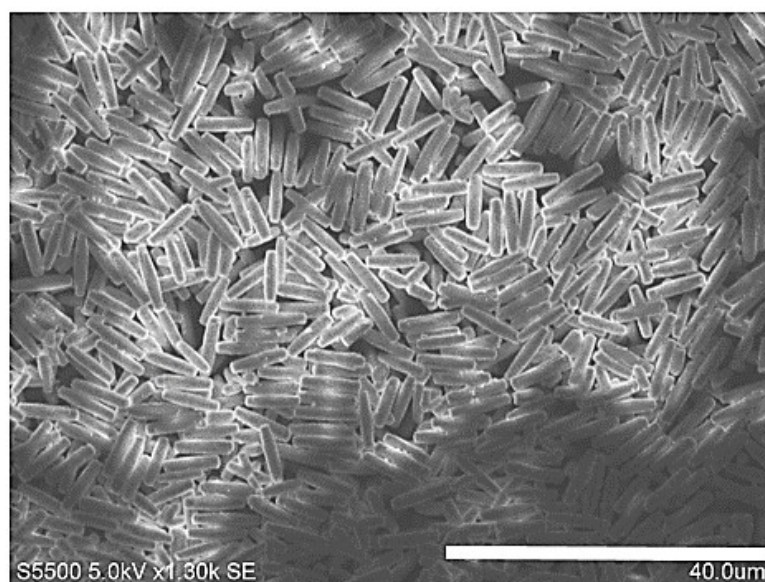


Fig. S18. SEM image of a spot of NU-1000/NEM on cotton paper