Supporting Information to Accompany

Photoactive Chelating Organic Nanospheres as Central Platforms of Bimodal Hybrid Nanoparticles

Contribution from

CEISAM – UMR CNRS 6230, Université de Nantes, 2 rue de la Houssinière, BP 92208, 44 322 Nantes cedex 3, France elena.ishow@univ-nantes.fr

A. Faucon, J. Fresnais, A. Brosseau, P. Hulin, S. Nedellec, J. Hémez and E. Ishow *

Table of Contents

- **1. Synthetic procedures**
- 2. Nanoparticle stability
- 3. Time-resolved fluorescence measurements
- 4. Magnetic experiments

List of Schemes, Figures and Tables

Scheme 1. General synthesis of the carboxylic acid fluorophore (C).

Scheme 2. General synthesis of the phosphonic acid fluorophore (P).

Figure S1. Evolution of the mean hydrodynamic diameter D_H of (P)-FON and (C)-FON as a function

of the concentration of the stock solution.

Figure S2. Lifetime decay of (P)-FON solution.

Figure S3. Lifetime decay of of (C)-FON solution.

Figure S4. Lifetime decay and microscope fluorescence imaging of (P)-fluo@mag NP solution.

Figure S5. Lifetime decay and microscope fluorescence imaging of (C)-fluo@mag NP solution.

Movie 1. Fluorescence recording of the migration of (P)-fluo@mag NP in the presence of a low magnitude magnet.

Experimental Section

1. Synthetic procedures

1.1. General

All chemical reagents and solvents were purchased from commercial sources (Aldrich, Acros, SDS) and used as received. Spectroscopic grade solvents purchased from Aldrich were used for spectroscopic measurements. All air-sensitive reactions were performed under argon using a vacuum line. Analytical TLC was performed on Kieselgel F-254 precoated plates. Visualization was done with UV lamp. Flash chromatography was carried out with silica gel 60 (230-400 mesh) from SDS and 4-bis(4'-tert-butylbiphenyl-4-yl)aminobenzaldehyde¹ was synthesized according to literature procedures. ¹H NMR, ¹³C NMR, ³¹P NMR spectra were recorded on Bruker 300 MHz or 400 MHz spectrometers. Chemical shifts δ were reported in ppm relative to TMS and referenced to the residual solvent. Low-resolution mass (LR-MS) spectra were obtained by electrospray ion trap mass spectrometry (LC-Esquire, Bruker) in positive-ion mode. High-resolution mass (HR-MS) spectra were obtained either by electrospray ionization coupled with high resolution ion trap orbitrap (LTQ-Orbitrap, ThermoFisher Scientific,) or by MALDI-TOF-TOF (Autoflex III de Bruker), both working in ion-positive mode.

1.2. Synthesis of the carboxylic acid fluorophore (C)



Scheme S1. i- Anhydrous ethyleneglycol, sodium, THF 0-40°C; ii- cyanoacetic acid, NH_4OAc , pyridine, 80°C, 16 h; iii- diisopropylcarbodiimide, 4-(dimethylamino)pyridinium 4-toluenesulfonate, CH_2Cl_2 , RT, 12 h; iv- CF_3SO_3H , RT, 2 h.

Tert-butyl 3-(2-hydroxyethoxy)propanoate 6^2 . To a solution of anhydrous ethylene glycol (2.540 g, 40.95 mmol, 3 eq.) in tetrahydrofurane was added oil-free sodium (9.4 mg, 0.41 mmol, 0.03 eq.). The resulting mixture was stirred for 2 h at room temperature and heated at 40 °C for a further 2.5 hours.

After cooling down to room temperature, *tert*-butylacrylate (1.75 g, 13.65 mmol, 1 eq.) was added. The reaction mixture was stirred at room temperature for an additional 18 h. After solvent removal under vacuum, the oily residue was washed with brine and extracted 6 times with ethyl acetate. The combined organic extracts were dried over anhydrous sodium sulfate. A crude colorless oil was obtained after solvent removal under reduced pressure. Purification by silica gel column chromatography with ethyl acetate: petroleum ether as an eluent (1:1) afforded *tert*-butyl 3-(2-hydroxyethoxy)propanoate **1** as a colorless oil (0.549 mg, 18%). ¹H NMR (300 MHz, CDCl₃): δ = 3.73 (t, ³*J*(H-H) = 6.2 Hz, 2H), 3.72 (t, ³*J*(H-H) = 4.8 Hz, 2H), 3.58 (t, ³*J*(H-H) = 4.8 Hz, 2H), 2.51 (t, ³*J*(H-H) = 6.2 Hz, 2H), 1.46 (s, 9H, *t*-Bu) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 171.4, 81.0, 72.0, 66.5, 61.7, 36.2, 28.2 ppm. HRMS (ESI+), *m/z* ([M+Na]⁺, 100%): for C₉H₁₈O₄Na calculated 213.1097, found 213.1101.

(*E*)-3-{4-[bis(4'-*tert*-butylbiphenyl-4-yl)amino]phenyl}-2-cyanopropen-2-oic acid 5. Under argon atmosphere, 4-[bis(4'-*tert*-butylbiphenyl-4-yl)amino]benzaldehyde 1 (500 mg, 0.93 mmol, 1 eq.) and cyanoacetic acid (118.7 mg, 1.395 mmol, 1.5 eq.) were dissolved in anhydrous pyridine (10 mL). Acetic acid (2 mL) and ammonium acetate (cat) were added, and the reaction mixture was heated at 80°C for 16 h. After cooling down to room temperature, the solution was poured into water (50 mL) under stirring to precipitate a red product. The product was filtered and thoroughly washed with water, and finally petroleum ether to yield **3** as a pure red powder (496 mg; 88%). T_g: 123 °C. ¹H NMR (400 MHz, DMSO): δ = 8.15 (s, 1H), 7.96 (d, ³*J*(H-H) = 9.1 Hz, 2H), 7.70 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.60 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.48 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.29 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.01 (d, ³*J*(H-H) = 9.1 Hz, 2H), 1.37 (s, 18H, *t*-Bu) ppm. ¹³C NMR (100 MHz, DMSO): δ = 164.0, 153.1, 151.4, 149.9, 144.3, 137.1, 136.4, 132.9, 130.1, 128.0, 126.5, 126.2, 125.7, 123.4, 119.0, 117.0, 98.5, 34.2, 31.1 ppm. UV-vis (toluene), λ_{max} (ε_{max} (mol⁻¹ L cm⁻¹) : 443 (2.17×10⁴), 327 (1.89×10⁴) nm, λ_{em} (Φ_f): 571 (0.18) nm. HRMS (MALDI-TOF), *m/z* (M⁺, 100%): for C₄₂H₄₀N₂O₂ calculated 604.3084, found 604.3070.

(*E*)-2-(3-(*tert*-butoxy)-3-oxopropoxy)ethyl 3-{4-[bis(4'-*tert*-butylbiphenyl-4-yl)amino]phenyl}-2cyanopropen-2-oate 7. To a solution of compound 5 (200 mg, 0.331 mmol, 1 eq.), 4-(dimethylamino)pyridinium 4-toluenesulfonate (48.7 mg, 0.166 mmol, 0.5 eq.) and compound 6 (64.9 mg, 0.331 mmol, 1 eq.) in anhydrous dichlorometane (23 mL) was slowly added *N*,*N*-Diisopropylcarbodiimide (83.5 mg, 0.662 mmol, 2 eq.) over 10 min. After stirring for 20 h at room temperature, the solution was concentrated under reduced pressure to provide a crude red solid. Purification by silica gel column chromatography with ethyl acetate: petroleum ether as an eluent (8:2) afforded compound 5 as a bright red solid (196 mg, 76%). T_g: 80 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.12 (s, 1H), 7.90 (d, ³*J*(H-H) = 8.6 Hz, 2H), 7.59-7.46 (m, 12H), 7.28-7.26 (m, 4H), 7.10 (d, ³*J*(H-H) = 8.6 Hz, 2H), 4.42 (t, ³*J*(H-H) = 4.7 Hz, 2H), 3.79-3.75 (m, 4H), 2.51 (t, ³*J*(H-H) = 6.5 Hz, 2H), 1.45 (s, 9H, *t*-Bu), 1.37 (s, 18H, *t*-Bu) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 170.9, 163.8, 154.3, 152.5, 150.6, 144.7, 138.1, 137.4, 133.4, 128.4, 126.7, 126.5, 126.0, 123.7, 119.7, 116.7, 97.2, 80.8, 68.7, 67.2, 65.4, 43.5, 36.4, 34.7, 31.5, 28.2, 22.7, 21.2 ppm. UV-vis (toluene), λ_{max} (ε_{max} (mol⁻¹ L cm⁻¹): 439 (2.88×10⁴), 330 (1.93×10⁴) nm, λ_{em} (Φ_f): 564 (0.19) nm. HRMS (MALDI-TOF), *m/z* (M⁺, 100%): for C₅₁H₅₆N₂O₅ calculated 776.4184, found 776.4156.

(E)-3-{2-[(3-{4-[bis(4'-*tert*-butylbiphenyl-4-yl)amino]phenyl}-2-cyanoacryloyl)oxy]ethoxy}

propanoic acid (C). A solution of compound **5** (170 mg, 0.219 mmol) in neat trifluoroacetic acid (10 mL) was stirred for 2h at room temperature. The dark red crude mixture was added to a large volume of cold water (100 mL) and extracted with ethyl acetate. The combined extracts were washed with sodium hydrogenocarbonate to remove the excess of trifluoroacetic acid. The organic layer was dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude red solid was purified by silica gel column chromatography with dichlorometane:methanol as an eluent (9.5:0.5) to give (C) as a red fluorescent solid (98 mg, 41 %). Tg: 100 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.11$ (s, 1H), 7.89 (d, ³*J*(H-H) = 9.1 Hz, 2H), 7.58 (d, ³*J*(H-H)= 8.6 Hz, 4H), 7.53 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.47 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.26 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.09 (d, ³*J*(H-H) = 9.1 Hz, 2H), 4.43 (t, ³*J*(H-H)= 4.8 Hz, 2H), 3.84 (t, ³*J*(H-H) = 5.9 Hz, 2H), 3.79 (t, ³*J*(H-H) = 4.8 Hz, 2H), 2.65 (t, ³*J*(H-H) = 5.9 Hz, 2H), 1.37 (s, 18H, *t*-Bu) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 163.8$, 154.5, 152.6, 150.6, 144.7, 138.4, 137.4, 133.5, 128.4, 126.7, 126.7, 126.0, 123.7, 119.7, 116.8, 97.1, 68.9, 66.8, 65.2, 34.7, 31.5, 29.9 ppm. UV-vis (toluene), λ_{max} (ε_{max} (mol⁻¹Lcm⁻¹): 445 (2.89×10⁴), 327 (1.98×10⁴) nm, λ_{em} (Φ_t): 569 (0.19) nm. HRMS (MALDI-TOF), *m/z* (M⁺, 100%): for C₄₇H₄₈N₂O₅ calculated 720.3558, found 720.3577.

1.3. Synthesis of the phosphonic acid fluorophore (P)



Scheme S2. i- PPh₃, CBr₄, THF, RT, 1h; ii- diisopropylcarbodiimide, 4-(dimethylamino)pyridinium 4toluenesulfonate, CH_2Cl_2 :THF 1:2, 0°C then RT, 12 h; iii- $P(OEt)_3$, 150°C, 12 h; iv- aldehyde derivative 2, NH₄OAc, pyridine, 60°C, 16 h; iV Me₃SiBr, CH₂Cl₂, RT, 12 h.

2-(2-bromoethoxy)ethanol 8³. To a solution of diethylene glycol (5 mL, 5.53 g, 52.1 mmol, 3 eq.) and triphenyphosphine (4.35 g, 16.6 mmol, 1 eq.). in anhydrous THF (10 mL), previously cooled with a water bath, was added carbon tetrabromide (5.5 g, 16.6 mmol, 1 eq.) portionwise to avoid overheating of the solution. The reaction mixture was allowed to stir at room temperature for 1 h. After solvent removal under vacuum, the crude oil was purified by silica gel chromatography with ethyl acetate:petroleum ether 1:1 as an eluent. A colorless oil was obtained in a 93 % yield (2.87 g). ¹H NMR (400 MHz, CDCl₃): δ = 3.82 (t, 2H, ³*J*(H,H) = 5.8 Hz), 3.75 (m, 2H, ³*J*(H,H) = 4.2 Hz), 3,62 (m, 2H, ³*J*(H,H) = 4.2 Hz), 3.49 (t, 2H, ³*J*(H,H) = 5.9 Hz) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 72.2, 71.0, 61.8, 30.6 ppm. LRMS (CI-NH₃), m/z ([M+NH₄]⁺, 100 %): for C₄H₉BrO₂NH₄ calculated 186.01, found 186.11.

2-(2-bromoethoxy)ethyl 2-cyanoethanoate 9. A solution of cyanoacetic acid (377.4 mg, 2.95 mmol, 1.5 eq.), 4-(dimethylamino)pyridinium 4-toluenesulfonate (434 mg, 1.47 mmol, 0.5 eq.) and 2-(2-bromoethoxy)ethanol **8** (500 mg, 2.95 mmol, 1 eq.) in tetrahydrofuran (15 mL) was cooled down to 0°C. A solution of *N*,*N*-diisopropylcarbodiimide (744 mg, 5.9 mmol, 2 eq.) in dichloromethane (30 mL) was added dropwise. The reaction mixture was allowed to stir at room temperature for 18 h. After solvent removal under reduced pressure, the crude yellow oil was purified by silica gel column chromatography with dichloromethane: petroleum ether as an eluent (99:1) to give compound **9** as a colorless oil (0.652 mg, 93%).¹H NMR (300 MHz, CDCl₃): δ = 4.40-4.37 (m, 2H), 3.82 (t, ³*J*(H-H) = 5.9 Hz, 2H), 3.78-3.75 (m, 2H), 3.51 (s, 2H), 3.47 (t, ³*J*(H-H) = 6.1 Hz, 2H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 163.0, 112.9, 71.2, 68.5, 65.7, 30.3, 24.5 ppm. LRMS (ESI+), *m/z* ([M+NH₄]⁺, 100%): for C₇H₁₀BrNO₃NH₄ calculated 253.01, found 253.15.

2-[2-(diethoxyphosphoryl)ethoxy]ethyl 2-cyanoethanoate 2. A solution of compound **9** (700 mg, 2.97 mmol, 1 eq.) and triethylphosphite (0.6 mL, 593 mg, 1.2 eq.) was deaerated and heated at 150°C during 16 h. After cooling down to room temperature, the crude mixture was purified by column chromatography with ethylacetate: petroleum ether as an eluent (1:1) to afford 2-(2-(diethoxyphosphoryl)ethoxy)ethyl 2-cyanoacetate 2 as a colorless oil (554 mg, 63%).¹H NMR (400 MHz, CDCl₃): δ = 4.34 (m, 2H), 4.09 (m, 6H), 3.73 (dt, ³*J*(H-H) = 7.4 Hz, ²*J*(H-P) = 12.4 Hz, 2H), 3.68 (m, 2H), 3.51 (s, 2H), 1.32 (t, ³*J*(H-H) = 7.0 Hz, 6H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 163.1, 113.0, 68.1, 65.6, 65.3, 61.8 (d, ²*J*(C-P) = 6 Hz), 27.0 (d, ¹*J*(C-P) = 140 Hz), 24.8, 16.5 ppm. LRMS (ESI+), *m/z* ([M+H]⁺, 100%): for C₁₁H₂₁NO₆P calculated 294.10, found 294.18.

(E)-2-[2-(diethoxyphosphoryl)ethoxy]ethyl 3-{4-[bis(4'-tert-butylbiphenyl-4-yl)amino]phenyl}-2-4. То of 4-(bis(4'-(tert-butyl)-[1,1'-biphenyl]-4cyanopropen-2-oate а solution yl)amino)benzaldehyde 1 (150 mg, 0.27 mmol, 1 eq.) and compound 2 (122.5 mg, 0.41 mmol, 1.5 eq.) in anhydrous pyridine (2 mL) were added glacial acetic acid (0.4 mL) and ammonium acetate (cat). The reaction mixture was heated at 60°C for 14 h. After cooling down to room temperature, the reaction mixture was poured into water (15 mL) and the crude red solid was filtered. Purification by silica gel column chromatography with dichloromethane: ethyl acetate as an eluent (30:70) afforded compound 4 as a red fluorescent solid (197 mg, 87 %). T_g : 66°C. ¹H NMR (400 MHz, CDCl₃): $\delta =$ 8.12 (s, 1H), 7.89 (d, ${}^{3}J$ (H-H) = 9.0Hz, 2H), 7.58 (d, ${}^{3}J$ (H-H) = 8.5Hz, 4H), 7.54 (d, ${}^{3}J$ (H-H) = 8.5Hz, 4H), 7.47 (d, ${}^{3}J(H-H) = 8.4Hz$, 4H), 7.27 (d, ${}^{3}J(H-H) = 8.5Hz$, 2H), 7.09 (d, ${}^{3}J(H-H) = 8.9Hz$, 2H), 4.44-4.42 (m, 2H), 4.13-4.09 (m, 4H), 3.80-3.75 (m, 4H), 2.13 (td, ${}^{3}J(H-H) = 7.3Hz$, ${}^{2}J(P-H) =$ 18.7Hz, 2H), 1.37 (s, 18H, *t*-Bu), 1.32 (t, 6H, ${}^{3}J(H-H) = 7.1Hz$) ppm. ${}^{13}C$ NMR (75.5 MHz, CDCl₃): δ= 171.4, 163.9, 154.6, 152.7, 150.7, 144.8, 138.5, 137.6, 133.6, 128.5, 126.8, 126.1, 123.8, 119.8, 116.9, 97.2, 68.7, 65.5 (d, ${}^{2}J(C-P) = 20$ Hz), 62.0 (d, ${}^{2}J(C-P) = 5$ Hz), 60.7, 34.8, 31.6, 27.3 (d, ${}^{1}J(C-P)$ = 139 Hz), 21.3, 16.7 (d, ${}^{3}J(C-P) = 5$ Hz), 14.5 ppm. ${}^{31}P$ NMR { ${}^{1}H$ } (160 MHz, CDCl₃): δ = 28.5 ppm. UV-vis (toluene), λ_{max} (ε_{max} (mol⁻¹Lcm⁻¹): 443 (3.74×10⁴), 325 (2.43×10⁴) nm, λ_{em} (Φ_{f}): 564 (0.22) nm. HRMS (MALDI-TOF), m/z ([M+Na]⁺, 100%): for C₅₀H₅₇N₂O₆PNa calculated 835.3846, found 835.3852.

(E)-(2-{2-[(3-{4-[bis(4'-(*tert*-butylbiphenyl-4-yl)amino]phenyl}-2-cyanoacryloyl)oxy]ethoxy}

ethyl)phosphonic acid (P). Trimethylsilyl bromide (118 mg, 0.76 mmol, 30 eq.) was added to a solution of compound **4** (20 mg, 0.02 mmol, 1 eq.) in anhydrous dichloromethane (0.6 mL). The reaction mixture was allowed to stir for 15 h at room temperature under argon atmosphere. Excess of trimethylsilyl bromide was removed during solvent evaporation under reduced pressure to give a crude red solid which was further dissolved in anhydrous methanol. After stirring for one hour at room temperature, the solution was again evaporated under vacuum. The resulting solid was dissolved in an excess of diethylether and acetone was added. The evaporation of diethylether under reduced pressure allows the phosphonic acid derivative (**P**) to precipitate as a pure red solid which was washed off several times with acetone (6.5 mg, 35%). T_g: 102 °C. ¹H NMR (400 MHz, MeOD): δ = 8.20 (s, 1H), 7.94 (d, ³*J*(H-H) = 9.1 Hz, 2H), 7.66 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.57 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.48 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.29 (d, ³*J*(H-H) = 8.6 Hz, 4H), 7.07 (d, ³*J*(H-H) = 9.1 Hz, 2H), 4.43 (t, ³*J*(H-H) = 4.8 Hz, 2H), 3.81-3.77 (m, 4H), 2.09 (td, ³*J*(H-H) = 7.7Hz, ²*J*(P-H) = 18.8Hz, 2H), 1.36 (s, 18H, *t*-Bu) ppm.³¹P NMR {¹H} (160 MHz, MeOD): δ = 21.8 ppm. UV-vis (toluene), λ_{max} (ε_{max} (mol⁻¹Lcm⁻¹): 442 (2.83×10⁴), 327 (2.70×10⁴) nm, λ_{em} (Φ_f): 572 (0.002) nm. HRMS (MALDI-TOF), *m/z* ([M+Na]⁺, 100%): for C₄₆H₄₉N₂O₆PNa calculated 779.3220, found 779.3247.

2. Nanoparticle stability



Figure S1. Evolution of the mean hydrodynamic diameter D_H of (**P**)-FON and (**C**)-FON as a function of the concentration of the stock solution (50 μ L) added into 2.5 mL of Millipore water.

3. Time-resolved fluorescence measurements

Fluorescence intensity decays were measured by the time-correlated single-photon counting method (TCSPC) with a femtosecond laser excitation at 450 nm provided by a Spectra-Physics setup composed of a Titanium-Sapphire Tsunami laser pumped by a doubled YAG laser (Millennia), pumped itself by a two-laser diode array, and doubling LBO crystals. Light pulses at 900 nm were selected by optoacoustic crystals at a repetition rate of 4 MHz, and then doubled at 450 nm. Fluorescence photons were detected at 580 nm through a monochromator by means of a Hamamatsu MCP R3809U photomultiplier, connected to a constant-fraction discriminator. The time-to-amplitude converter was from Tennelec. Pulse deconvolution was performed from the time profile of the exciting pulse recorded under the same conditions by using a Ludox solution. The fluorescence data were analyzed by a nonlinear least-squares global method using the Globals software package developed at the Laboratory for Fluorescence Dynamics at the University of Illinois at Urbana-Champaign (Globals software, Irvine, CA, USA). The fit quality was assessed by the residuals, namely the difference between the measured and fitted values, divided by the square root of the fit. χ^2 is equal to the variance of the weighted residuals. A fit was regarded as appropriate for χ^2 values comprised between 0.8 and 1.2.



Figure S2. Fluorescence lifetime decay of a (**P**)-FON solution in acidic water (pH = 1.4, HNO_3) and multiexponential fit ($\chi^{(2)} = 1.18$) showing three major time constants at $\tau_1 = 1.49$ ns ($f_1 = 0.07$), $\tau_2 = 0.63$ ns ($f_2 = 0.43$), and $\tau_3 = 0.20$ ($f_3 = 0.42$) with f_i designating the time fractional intensity.



Figure S3. Fluorescence lifetime decay of a (C)-FON solution in acidic water (pH = 1.4, HNO_3) and multiexponential fit ($\chi^{(2)} = 1.10$) showing three major time constants at $\tau_1 = 2.81$ ns ($f_1 = 0.24$), $\tau_2 = 1.00$ ns ($f_2 = 0.52$), and $\tau_3 = 0.25$ ($f_3 = 0.20$) with f_i designating the time fractional intensity. with f_i designating the time fractional intensity.



Figure S4. Microscope fluorescence imaging of (**P**)-fluo@mag NPs upon excitation at 488 nm. Left: Fluorescence lifetime decay and multiexponential fit ($\chi^{(2)} = 1.18$) showing three major time constants at $\tau_1 = 0.77$ ns ($f_1 = 0.34$), $\tau_2 = 0.24$ ns ($f_2 = 0.48$), and $\tau_3 = 0.08$ ($f_3 = 0.14$) with f_i designating the time fractional intensity. Right: fluorescence imaging (4 µm×4µm).



Figure S5. Microscope fluorescence imaging of (C)-fluo@mag NPs upon excitation at 488 nm. Left: Fluorescence lifetime decay and multiexponential fit ($\chi^{(2)} = 1.09$) showing three major time constants at $\tau_1 = 2.37$ ns ($f_1 = 0.24$), $\tau_2 = 0.81$ ns ($f_2 = 0.48$), and $\tau_3 = 0.20$ ($f_3 = 0.23$) with f_i designating the time fractional intensity. Right: fluorescence imaging (4 μ m×4 μ m).

4. Magnetic experiments

Migration of magnetofluorescent nanoparticles was followed by fluorescence microscopy ($\lambda_{exc} = 488$ nm) in the presence of a magnet (B < 1mTesla) placed close to the stage supporting a drop of fluo@mag nanoparticles made of citrate-coated maghemite nanoparticles.

Movie 1. The movie shows two deflections of a random motion of a fluo@mag NP when approaching a magnet first in the bottom right-hand corner, and a few seconds later in the up left-hand corner (see attached file : movie1_fluo@mag).

References

- (1) E. Ishow, A. Brosseau, G. Clavier, K. Nakatani, P. Tauc, C. Fiorini-Debuisschert, S. Neveu, O. Sandre and A. Leaustic, *Chem. Mater.* 2008, **20**, 6597-6599.
- (2) Z. Li, D. Yang, R. Gabather and Q. Chen, Synth. Commun. 2007, 37, 1899-1915.
- (3) W.-S. Yeo, D.-H. Min, R. W. Hsieh, G. L. Greene and M. Mrksich, *Angew. Chem. Int. Ed.* 2005, 44, 5480-5483.