Supporting Information

Tuning the excited-state dynamics of GFP-inspired imidazolone derivatives

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1) Synthesis.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DRX-250 spectrometer (^{1}H at 250.1 MHz, ^{13}C at 62.9 MHz) and Bruker Avance II+ 600 spectrometer (600.13 for ^{1}H, 150.92 MHz and for ^{13}C NMR) using tetramethylsilane (^{1}H) as an internal standard. ^{1}H and ^{13}C NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), integration, identification, and coupling constants (Hz). In ^{13}C NMR spectra the singlet C-signals are not assigned with letter. Mass spectra (MS) analyses were obtained with a Hewlett Packard Mass Selective Spectrometer HP 5973 by electron ionization (EI) at 70 eV; fragmentations in m/z with relative intensities (%) in parentheses. Elemental analyses were performed by the Microanalytical Laboratory for Elemental Analysis of the Institute of Organic Chemistry,

Bulgarian Academy of Sciences. Melting points were obtained using an Electrothermal MEL-TEMP apparatus (uncorrected). TLC analyses were performed by means of Merck Kieselgel 60 F_{254} (0.25 mm) Plates. Visualization was accomplished with UV light (254 and 366 nm). Flash column chromatography was carried out using Silica Gel 60 230-400 mesh (Fluka). The following commercially available reagents were used without purification: hippuric acid (97%, Fluka), acetic anhydride Ac_2O (reagent grade 98%, Sigma-Aldrich), anhydrous potassium acetate KOAc (purum p.a. 99%, Fluka), glacial acetic acid (Sigma-Aldrich), benzaldehyde (Acros), 4-hydroxybenzaldehyde (Acros), biphenyl-4-carboxaldehyde (Aldrich), aniline (Acros), 4-dimethylaminobenzaldehyde (Acros), 2-aminophenol (Acros). Commercially available solvents for column chromatography and crystallization were used after distillation.

General procedure 1: Preparation of (*Z*)-2-phenyl-4-(arylmethylene)oxazol-5(4*H*)-ones **IIIa**-**d** (Scheme 1A):

A mixture of hippuric acid **I** (2.00 g, 11.2 mmol), aldehyde **IIa**-**d** (11.2 mmol) and anhydrous KOAc (1.10 g, 11.2 mmol) was refluxed in 15 ml Ac_2O for 1 h. After cooling the volatiles were evaporated *in vacuo* to obtain the crude solid product **IIIa**-**d**. This solid was washed with 15 ml hexane in ultrasound bath and crystallized from 40 ml EtOH/water. The purity of the oxazolones **IIIa**-**d** was checked by TLC and they were used for further reactions without characterization.

Yield of the products: **IIIa** – 32% (yellow crystals after crystallization from EtOH/water 1:1 v/v), **IIIb** – 75% (yellow crystals after crystallization from EtOH/water 3:1 v/v), **IIIc** – 44% (yellow-orange crystals after crystallization from EtOH/water 5:1 v/v), **IIId** – 55% (purple crystals after crystallization from EtOH/water 1:1 v/v).

General procedure 2: Preparation of (*Z*)-2-phenyl-1-(aryl)-4-(arylmethylene)-1*H*-imidazol-5(4*H*)-ones **1**-**5** (Scheme 1B):

A mixture of oxazolone **IIIa**-**d** (5.0 mmol), arylamine **IVa**-**b** (20.0 mmol) and anhydrous KOAc (5.0 mmol) was refluxed in glacial acetic acid (20 ml) for 7 h. After cooling the volatiles were evaporated *in vacuo*. The residue was washed with 50 ml hexane in ultrasound bath and dried *in vacuo* to obtain the crude product **1**-**5**.

(*Z*)-4-benzylidene-1,2-diphenyl-1*H*-imidazol-5(4*H*)-one **1**

The crude **1** was obtained from **IIIa** and **IVa** according to General procedure 2. It was crystallized from EtOH/H_2O = 1:1 v/v. The crystals were additionally washed with water, dried and purified by column chromatography (80 g silica gel, phase CH_2Cl_2/hexane = 1:1) to give 0.62 g (38%) of **1** as yellow crystals. Mp. 176-178 ºC (lit. 178-179 ºC,[63] 186-188 ºC[73]). ^{1}H NMR (600.13 MHz, $CDCl_3$) δ 8.30 (m, 2H, arom.), 7.58 (m, 2H, arom.), 7.37-7.49 (m, 7H, arom.), 7.34 (s, 1H, H-9), 7.32 (m, 2H, arom.), 7.19 (m, 2H, arom.). ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 170.51 (1C, quaternary C-imidazolone), 160.52 (1C, quaternary C-imidazolone), 138.52 (1C, quaternary), 134.62 (1C, quaternary), 134.30 (1C, quaternary), 132.60 (2C, CH), 131.36 (1C, CH), 130.47 (1C, CH), 129.39 (2C, CH), 129.36 (1C, C-9), 129.23 (2C, CH), 128.76 (2C, CH), 128.31 (1C, CH), 128.30 (2C, CH), 127.27 (2C, CH). MS (EI) m/z (%): 324 ($M^{+\bullet}$, 100), 181 (15), 180 (77), 105 (69), 77 (60), 51 (17). Anal. calcd. for $C_{22}H_{16}N_2O$ (324.38): C, 81.46; H, 4.97; N, 8.64; O, 4.93. Found: C, 81.40; H, 4.91; N, 8.69%.

(*Z*)-4-(4-hydroxybenzylidene)-1,2-diphenyl-1*H*-imidazol-5(4*H*)-one **2**

The crude **2** was obtained from **IIIc** and **IVa** according to General procedure 2. It was than refluxed for 30 min in suspension of 0.5 g $NaHCO_3$ in 50 ml EtOH/H_2O = 1:1 v/v. After cooling the mixture was neutralized with citric acid (pH 5) and evaporated *in vacuo*. The residue was crystallized from EtOH/H_2O = 1:1 v/v. The crystals were washed with water, dried and than purified twice by column chromatography (190 g silica gel, phase CH_2Cl_2/MeOH = 10:1) to give 0.95 g (56%) of **2** as yellow crystals. Mp. 256-257 ºC; MS (EI) m/z (%): 340 ($M^{+\bullet}$, 100), 181 (22), 180 (94), 105 (63), 77 (65), 51 (17). Anal. calcd. for $C_{22}H_{16}N_2O_2$ (340.37): C, 77.63; H, 4.74; N, 8.23; O, 9.40. Found: C, 77.69; H, 4.77; N, 8.28%.

(*Z*)-4-(biphenyl-4-ylmethylene)-1,2-diphenyl-1*H*-imidazol-5(4*H*)-one **3**

The crude **3** was obtained from **IIIb** and **IVa** according to General procedure 2 and purified twice by column chromatography (190 g silica gel, phase CH_2Cl_2) to give 1.00 g (50%) of **3** as yellow crystals. Mp. 229-230 ºC. ^{1}H NMR (250.1 MHz, $CDCl_3$) δ 8.37 (m, 2H, H-2``, H-6``), 7.56-7.73 (overlapping m, 6H), 7.37 (s, 1H, H-9), 7.28-7.50 (overlapping m, 9H), 7.16-7.21 (m, 2H, H-2`, H-6`). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.43 (1C, quaternary C-imidazolone), 160.37 (1C, quaternary C-imidazolone), 142.93 (1C, quaternary), 140.22 (1C, quaternary), 138.51 (1C, quaternary), 134.69 (1C, quaternary), 133.41 (1C, quaternary), 133.08 (2C, C-2`, C-6`), 131.32 (1C, CH), 129.36 (2C, CH), 129.23 (2C, CH), 128.86 (2C, CH), 128.83 (1C, CH), 128.80 (1C, C-9), 128.28 (3C, CH), 127.86 (1C, CH), 127.33 (2C, CH), 127.29 (2C, C-2``, C-6``), 127.08 (2C, CH). MS (EI) m/z (%): 400 ($M^{+\bullet}$, 100), 181 (10), 180 (59), 105 (31), 77 (31). Anal. calcd. for $C_{28}H_{20}N_2O$ (400.47): C, 83.98; H, 5.03; N, 7.00; O, 4.00%. Found: C, 83.90; H, 4.99; N, 6.96%.

(*Z*)-4-(biphenyl-4-ylmethylene)-1-(2-hydroxyphenyl)-2-phenyl-1*H*-imidazol-5(4*H*)-one **4**

The crude **4** was obtained from **IIIb** and **IVb** according to General procedure 2 and purified twice by column chromatography (190 g silica gel, phase CH_2Cl_2/Et_2O 30:1) to give 0.44 g (21%) of **4** as yellow crystals. Mp. 217-218 ºC. ^{1}H-NMR (250.1, $CDCl_3$) δ 9.10 (br s, OH), 8.29 (d, 2H, H-2``, H-6``), 7.56-7.68 (overlapping m, 6H), 7.17-7.44 (overlapping m, 8H), 7.01 (dd, 1H), 6.79-6.93 (m, 2H). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 171.51 (1C, quaternary C-imidazolone), 161.13 (1C, quaternary C-imidazolone), 152.86 (1C, C-12), 142.87 (1C, quaternary), 140.05 (1C, quaternary), 138.45 (1C, quaternary), 133.20 (1C, C-1), 132.97 (2C, C-2`, C-6`), 131.18 (1C, CH), 130.37 (1C, CH), 129.15 (1C, CH), 128.99 (1C, CH), 128.75 (2C, C-2``, C-6``), 128.46 (2C, CH), 128.11 (2C, CH), 127.76 (1C, CH), 127.19 (2C, CH), 126.92 (2C, CH), 121.94 (1C, C-11), 120.10 (2C, CH), 117.12 (2C, CH). MS (EI) m/z (%): 416 ($M^{+\bullet}$, 100), 196 (47), 192 (13), 167 (11), 165 (10), 105 (81), 104 (19), 77 (17). Anal. calcd. for $C_{28}H_{20}N_2O_2$ (416.47): C, 80.75; H, 4.84; N, 6.73; O, 7.68 %. Found: C, 80.66; H, 4.93; N, 6.81%.

(*Z*)-4-(4-(dimethylamino)benzylidene)-1,2-diphenyl-1*H*-imidazol-5(4*H*)-one **5**

The crude **5** was obtained from **IIId** and **IVa** according to General procedure 2 and purified twice by column chromatography (190 g silicagel, phase CH_2Cl_2) to give 0.89 g (45%) of **5** as orange-red crystals. Mp. 250-251 ºC (lit. 250-252 ºC).[69,72] ^{1}H-NMR (250.1 MHz, $CDCl_3$) δ 8.23 (d, 2H, 2`-H, 6`-H, J = 9.0 Hz), 7.53-7.57 (overlapping m, 2H), 7.25-7.42 (overlapping m, 7H), 7.16-7.21 (overlapping m, 2H), 6.74 (d, 2H, 3`-H, 5`-H, J = 9.0 Hz), 3.08 (s, 6H, NMe_2). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.41 (1C, quaternary C-imidazolone), 157.05 (1C, quaternary C-imidazolone), 151.82 (1C, quaternary), 135.23 (1C, quaternary), 134.83 (2C, CH), 134.59 (1C, CH), 130.95 (1C, CH), 130.54 (1C, CH), 129.52 (2C, CH), 129.00 (2C,

CH), 128.16 (2C, CH), 127.95 (1C, CH), 127.40 (2C, CH), 122.59 (1C, CH), 111.80 (2C, CH), 40.04 (2C, NMe_2). MS (EI) m/z (rel. int.): 367 ($M^{+\bullet}$, 100), 181 (20), 180 (90), 159 (17). Anal. calcd. for $C_{24}H_{21}N_3O$ (367.44): C, 78.45; H, 5.76; N, 11.44; O, 4.35 %. Found: C, 78.54; H, 5.81; N, 11.39%.

2) Fluorescence decay in a solid matrix.

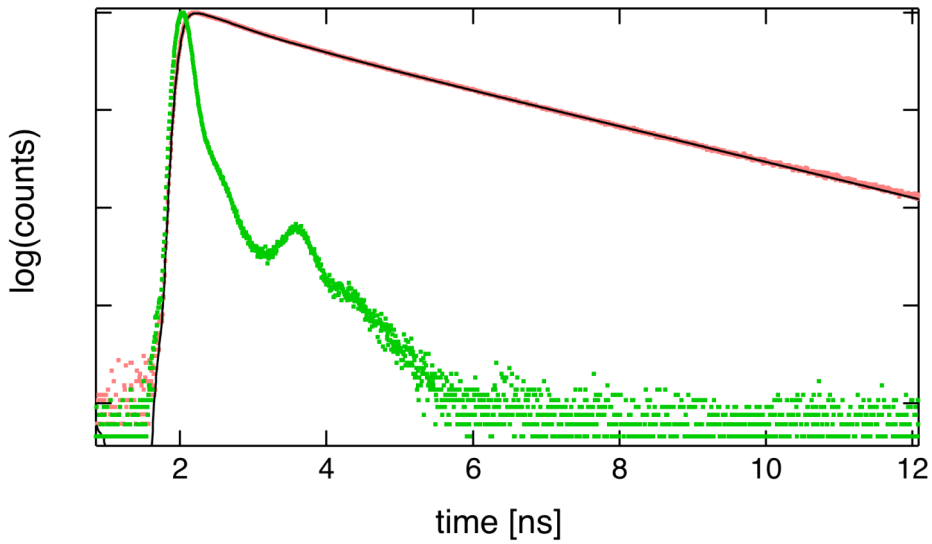

Figure S1: Decay of the fluorescence intensity of **2** in PMMA measured at 450 nm by TCSPC.

3) Temperature dependence.

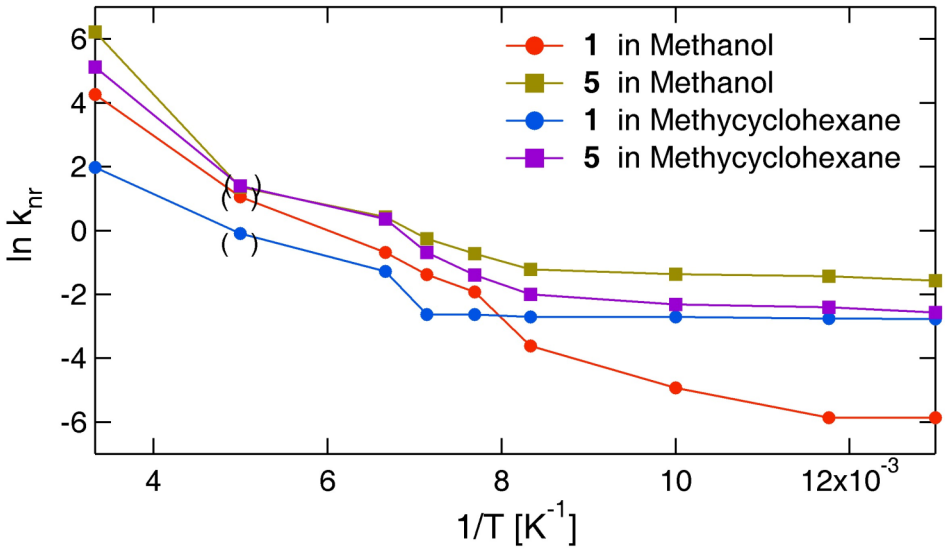

Figure S2: Arrhenius plots of the rate constants of non-radiative deactivation of **1** and **5** in methanol and methylcyclohexane deduced from TCSPC measurements (except at room temperature where they were determined from up-conversion measurements).

The parantheses denotes values where the fluorescence decay times were close to the IRF of the TCSPC setup.

4) Transient absorption.

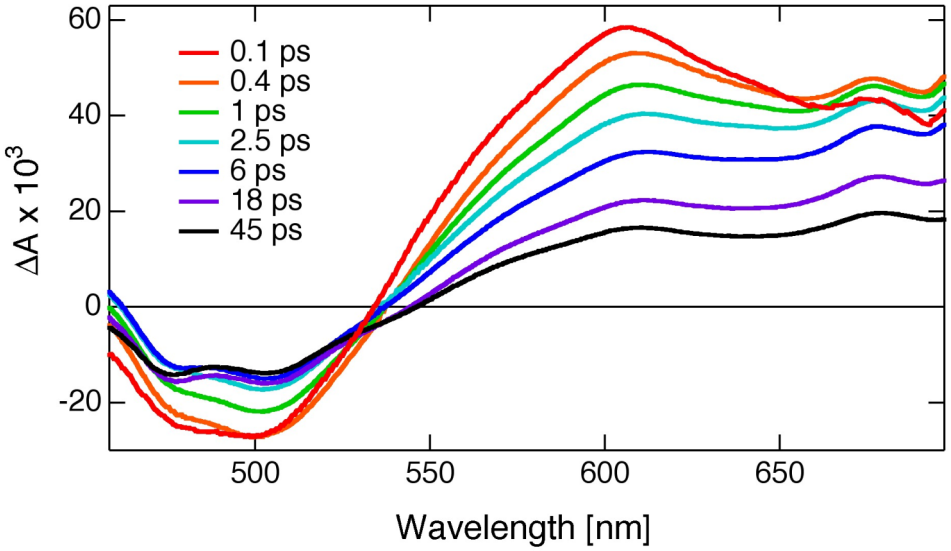

Figure S3: TA spectra recorded with **3** in cyclohexane at different time delays after excitation.