Supplementary information

1-Pyrenyl ynones: synthesis *via* a Friedel-Crafts route, electronic and molecular structure and fluorescence properties

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(S1) Syntheses.

Solvents were purified before use by reported methods. All reagents were purchased from Sigma-Aldrich and used without further purification Chromatographic separations were performed. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a *Bruker ARX 600 MHz* (600 MHz for ^{1}H and 151 MHz for ^{13}C). Chemical shifts were referenced relative to solvent signals: $\delta = 7.27$ ppm for ^{1}H and $\delta = 77.20$ ppm for [13]C. Spectra were recorded at room temperature (291 K), chemical shifts are in ppm and coupling constants in Hz. IR spectra were run on a FT-IR Nexus spectrometer in KBr pellets. Column chromatography was carried out on silica gel 60 (0.040-0.063 mm, 230-400 mesh, Fluka). Elemental analyses were performed in Laboratory of Microanalysis at The Centre of Molecular and Macromolecular Studies in Łódź, Poland.

Preparation of 1a-c

A solution of an alkynoic acid (1.1 mmol) and TFAA (153 µl,1.1 mmol) in dichloromethane (5 ml) was stirred 1 min at rt. and pyrene (202.5 mg, 1 mmol) and TfOH (97 µl, 1.1 mmol) were added. The resulting solution was stirred for 2 h. Water (15 ml) was added, the organic layer was separated and aqueous layer extracted with dichloromethane. The combined organic extracts were washed with water, dried ($MgSO_4$) and the solvent evaporated. Column chromatography (silica gel/dichloromethane) afforded corresponding pyrenyl ynone.

1-(Pyren-1-yl)but-2-yn-1-one (1a). Prepared using butyn-2-oic acid. Yield 198 mg (74%). Yellow solid. Mp 159-161°C. ^{1}H NMR: 9.51 (d, J= 9.4, 1H, CH), 8,95 (d, J= 8.1, 1H, CH), 8.30-8.27 (m, 3H, 3xCH), 8.22 (d, J=2.7, 1H, CH), 8.20 (d, J=1.8, 1H, CH), (q, J= 7.7, 2H, 2xCH), 2,23 (s, 3H, CH$_3$). ^{13}C NMR: 180.22, 135.15, 131.53, 131.01, 130.85, 130.58, 130.51, 130.44, 129.39, 127.14, 126.83, 126.60, 126.47, 124.97, 124.84, 124.12, 123.96, 91.65, 81.31, 4.46. IR (cm^{-1}): 3439, 3039, 2958, 2912, 2221, 2212, 1629, 1617, 1594, 1580 , Elemental Analysis Calcd for $C_{20}H_{12}O$, C- 89.53, H-4.51. Found: C-89.73 H-4.61.

3-Phenyl-1-(pyren-1-yl)prop-2-yn-1-one (1b). Prepared using 3-phenylpropiolic acid. Yield 228 mg (69%). Yellow solid. Mp 119-121°C. ^{1}H NMR: 9.56 (d, J = 9.3, 1H, CH), 9.03 (d, J = 8.2, 1H, CH), 8.32-8.27 (m, 3H, 3xCH), 8.23 (dd, J = 8.5, J= 5.2, 2H, 2xCH), 8.09 (q, J = 8.2H, 2H, 2xCH), 7.75 (d, J = 7.1 2H, 2xCH), 7.51-7.44 (m, 3H 3xCH). ^{13}C NMR: 179.97, 135.30, 133.00, 131.40, 131.39, 131.01, 130.95, 130.72, 130.60, 130.57, 130.52, 129.45, 128.67, 127.16, 126.94, 126.70, 126.52, 124.94, 124.93, 124.86, 124.09, 124.07, 120.60,

92.36, 89.27 IR (cm^{-1}):3448, 3042, 2196, 1894, 1628, 1614, 1590,1581, Elemental Analysis Calcd for C$_{25}$H$_{14}$O: C- 90.89, H-4.27. Found: C-90.71 H-4.51.
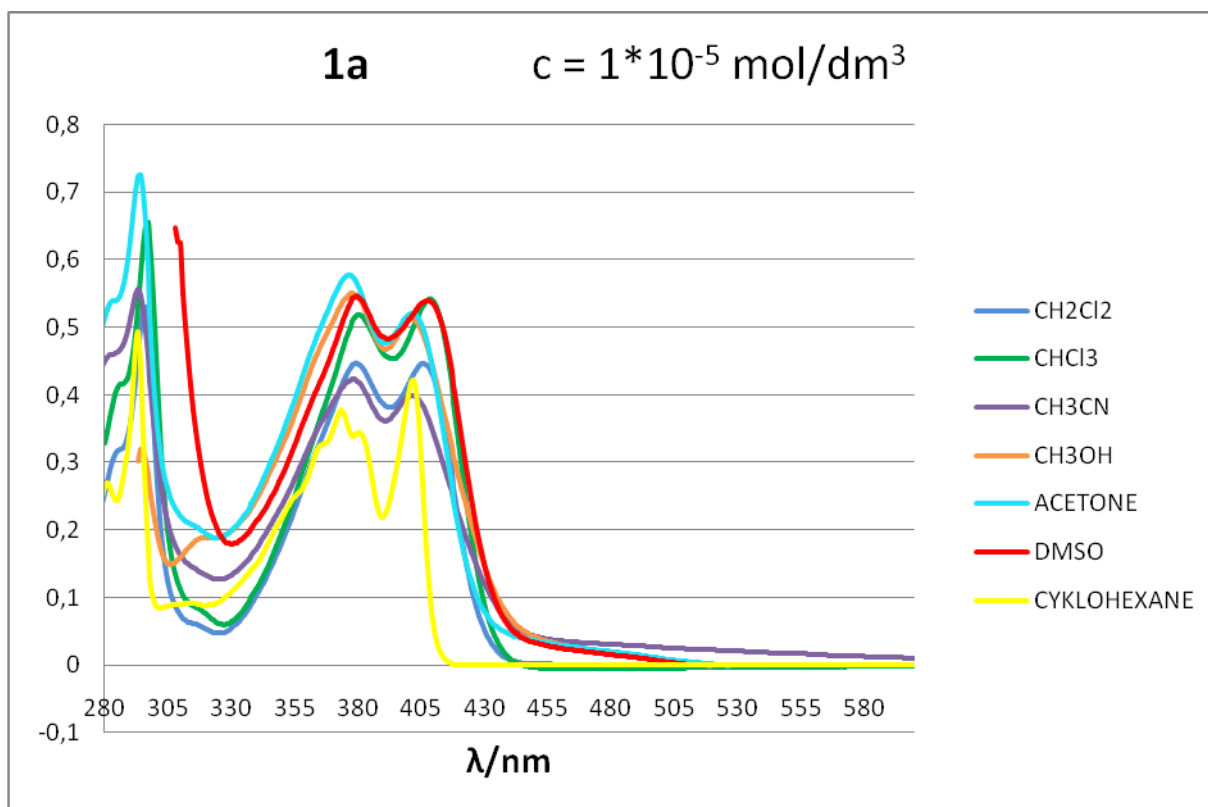
1-(Pyren-1-yl)-3-(trimethylsilyl)prop-2-yn-1-one (1c). Prepared using 3-(trimethylsilyl)propionic acid. Yield 235 mg (72%). Yellow solid. Mp 109-110°C. ^{1}H NMR: 9.47 (d, J = 9.4, 1H, CH), 8.92 (d, J = 8.2, 1H, CH), 8.23-8.19 (m, 3H, 3xCH), 8.15 (d, J=7.6, 1H, CH), 8.12 (d, J =8.8, 1H, CH), 8.04-7.97 (m, 2H, 2xCH), 0.41 (s, 9H, 3xCH$_3$) ^{13}C NMR: 179.56, 135.36, 131.69, 130.99, 130.74, 130.62, 130.49, 128.94, 127.37, 127.14, 126.95, 126.72, 126.51, 125.84, 124.92, 124.79, 124.04, 103.15, 99.04, 0.02.IR (cm^{-1}): 3439, 3043, 2958, 2924, 2852, 2146, 1630, 1617, 1593, Elemental Analysis Calcd for C$_{22}$H$_{18}$OSi, C-80.94, H-5.56. Found: C-80.81 H-5.64.
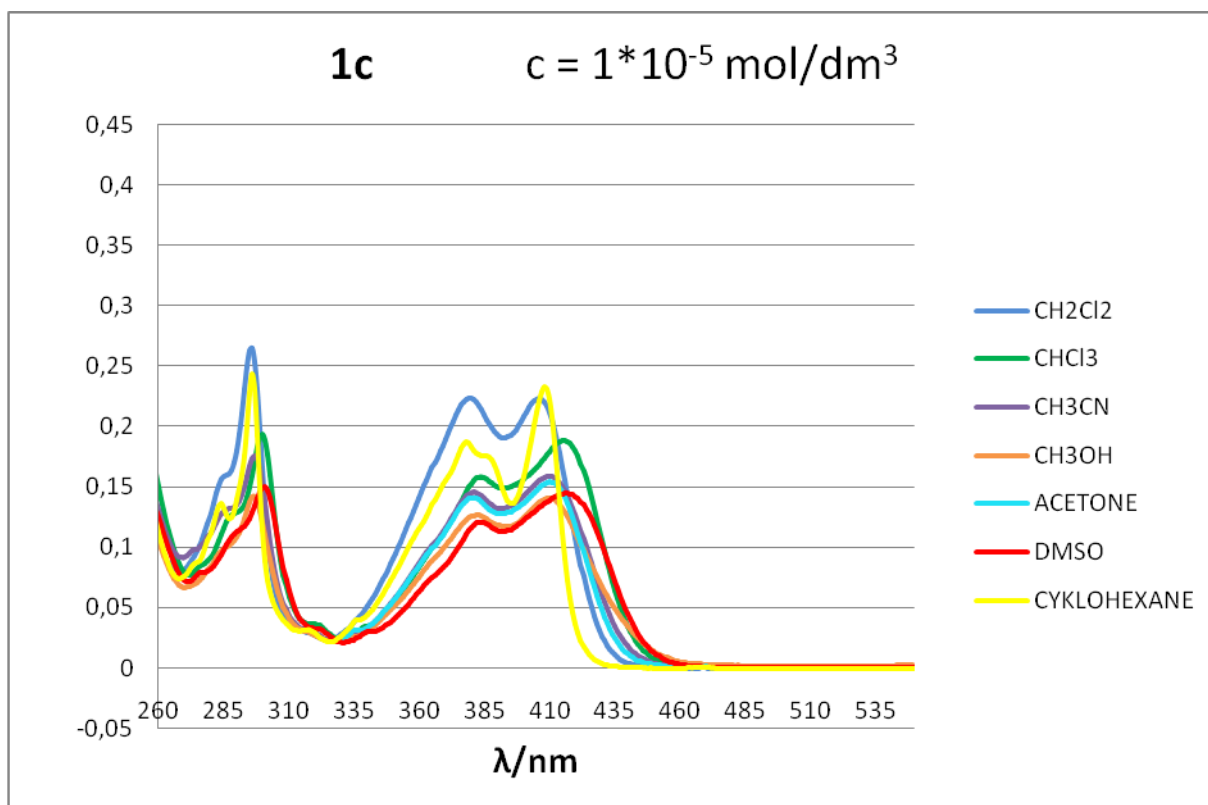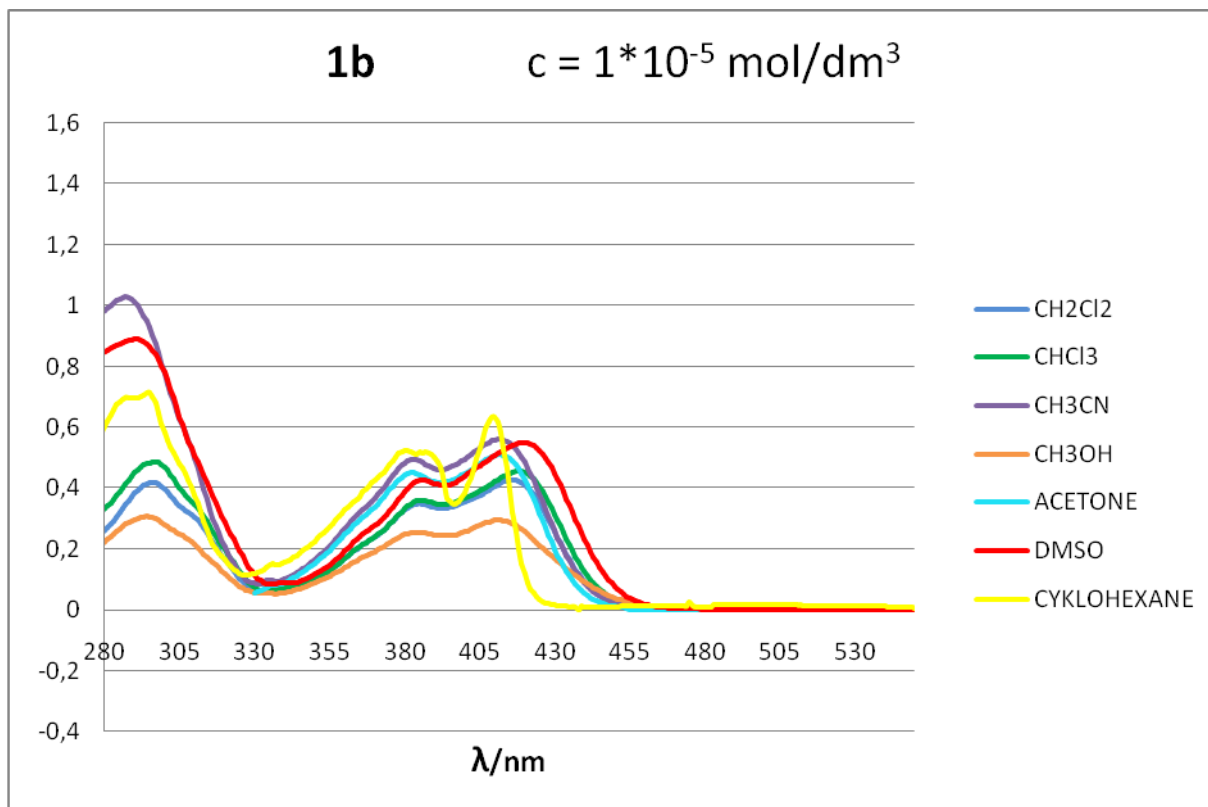
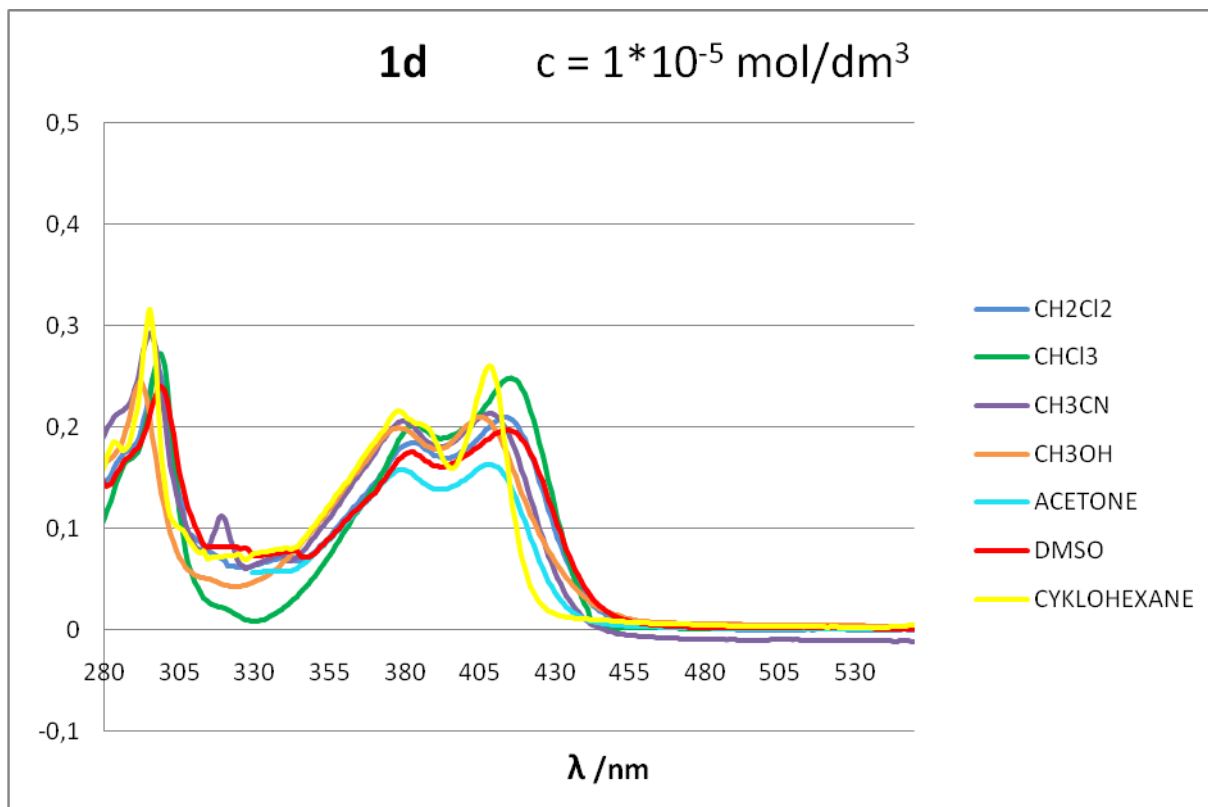**Preparation of 1-(pyren-1-yl)prop-2-yn-1-one (1d).**

To a solution of **1c** (163mg, 0.5 mmol), and 18-crown-6 (5 mg) in THF (10 ml), powdered anhydrous KF (700 mg, 12.0 mmol) was added at room temperature and the resulting mixture was stirred 30 min. After addition of water (30 ml) the product was extracted with dichloromethane (2 x 25 ml). The combined organic extracts were dried (MgSO$_4$) and the solvent evaporated. Column chromatography (dichloromethane as eluent) afforded **1d**. Yield 126 mg (99%).Yellow solid. Mp 138-139°C. ^{1}H NMR: 9.54 (d, J = 9.5, 1H, CH), 9.01 (d, J = 8.5, 1H, CH), 8.36-8.32 (m, 3H, 3xCH), 8.23 (dd, J.= 5.8, J = 4.5, 2H, 2xCH), 8.11-8.08 (m, 2H, 2xCH). 3.55 (s, 1H). ^{13}C NMR: 179.06, 135.65, 132.02, 132.03, 131.13, 131.07, 130.95, 130.87, 130.45, 128.23, 127.15, 127.11, 126.88, 126.60, 124.79, 124.06, 123.97, 82.39, 79.92. IR (cm^{-1}): 3423, 3215, 3035, 2962, 2923 2853, 2088, 1635, 1619, 1594, Elemental Analysis Calcd for C$_{19}$H$_{10}$O, C- 89.76, H-3.94. Found: C-89.57 H-4.12.

(S2) Electronic absorption and emission spectra

Electronic Absorption spectra of compounds 1a-d in various solvents

1b c = 1*10⁻⁵ mol/dm³

Chart 1b: UV-Vis absorption spectra, absorbance vs λ/nm (280–530 nm), y-axis from -0,4 to 1,6. Legend: CH2Cl2, CHCl3, CH3CN, CH3OH, ACETONE, DMSO, CYKLOHEXANE.

1c c = 1*10⁻⁵ mol/dm³

Chart 1c: UV-Vis absorption spectra, absorbance vs λ/nm (260–535 nm), y-axis from -0,05 to 0,45. Legend: CH2Cl2, CHCl3, CH3CN, CH3OH, ACETONE, DMSO, CYKLOHEXANE.

Fluorescence emission spectra of compounds 1a-d in various solvents
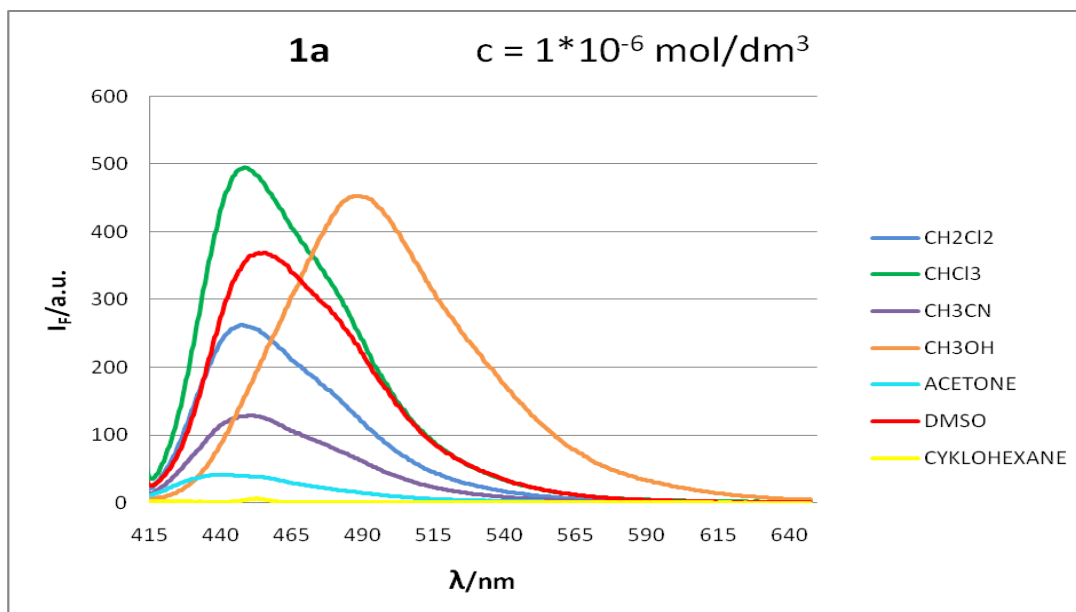
1b   c = 1*10⁻⁶ mol/dm³

1c   c = 1*10⁻⁶ mol/dm³
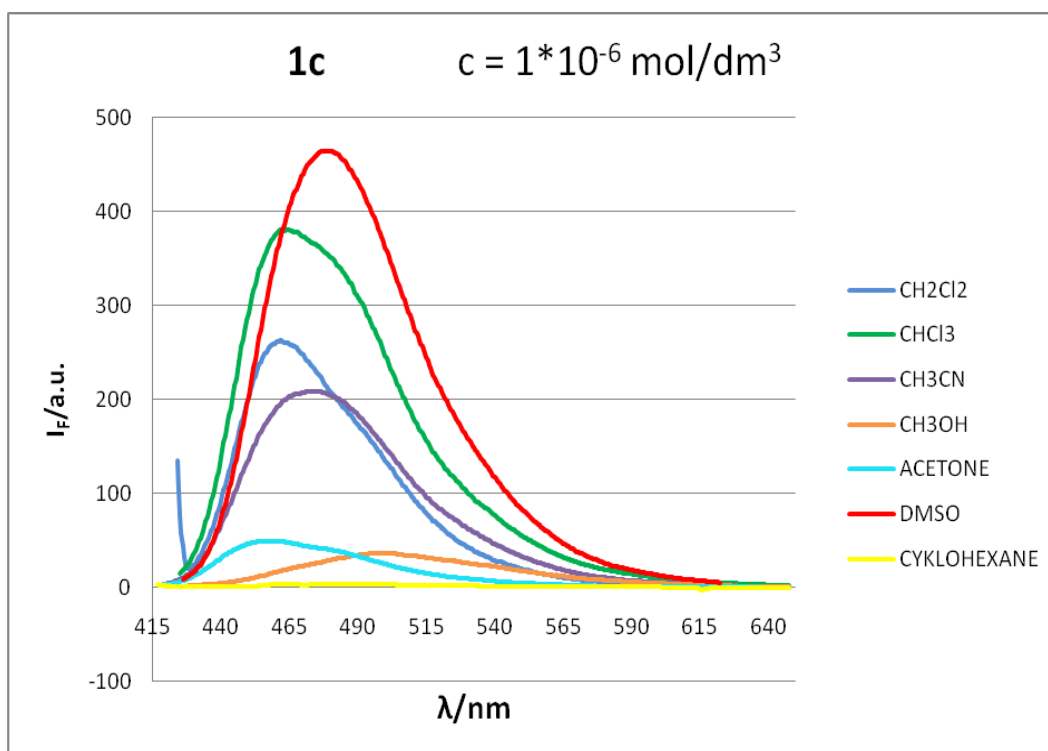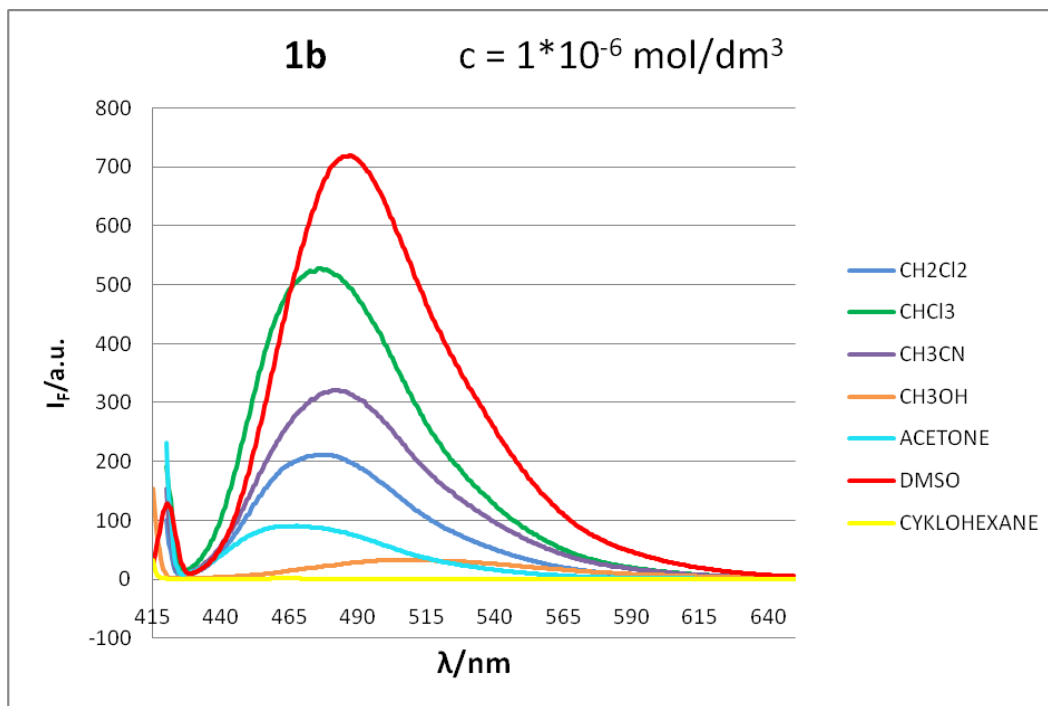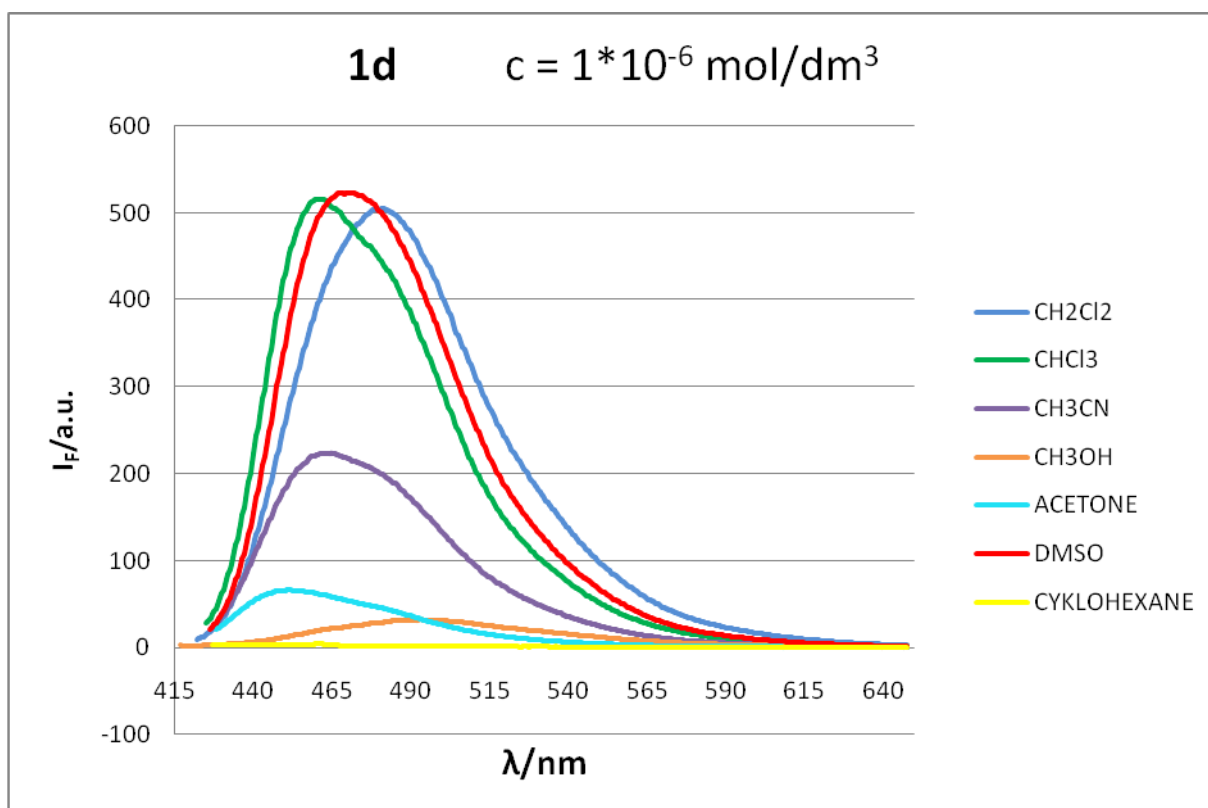
Fluorescence emission spectra of compounds 1a-d in various solvents

Excitation wavelengths

solvent	compound/ excitation λ [nm]			
	1a	**1b**	**1c**	**1d**
CH2Cl2	406	415	414	412
CHCl3	409	418	415	415
CH3CN	404	416	409	408
CH3OH	402	410	410	407
DMSO	410	425	416	415
ACETONE	404	411	409	408
CYKLOHEXANE	401	409	408	407

(S3) Photophysical study

Corrected emission spectra were obtained on a Fluorolog FL3-221 spectrofluorometer from Horiba Jobin-Yvon, including an integration sphere accessory which allows recording excitation and emission spectra and determining absolute quantum yield values in the powder state.

Fluorescence decay curves were obtained by the time-correlated single-photon counting (TCSPC) method with femtosecond laser excitation using a Spectra-Physics set-up composed of a Titanium Sapphire laser (Tsunami, Spectra-Physics) pumped by a doubled YAG laser (Millennia, Spectra-Physics), pumped itself by two laser diode arrays. Light pulses at 780 nm, for solution samples (resp. 740 nm for powder samples), were selected by optoacoustic crystals at a repetition rate of 4 MHz, and then doubled at 390 nm (resp. 370 nm) by non-linear crystals. Fluorescence photons were detected through a monochromator by means of a Hamamatsu MCP R3809U photomultiplier, connected to a constant-fraction discriminator. The time-to-amplitude converter was purchased from Tennelec. The instrumental response function was recorded before each decay measurement. The fluorescence data were analyzed using the Globals software package developed at the Laboratory for Fluorescence Dynamics at the University of Illinois at Urbana-Champaign, which includes reconvolution analysis and global non-linear least-squares minimization method.

(S4) DFT calculations

The geometry optimizations for all of the calculated compounds were performed using B3PW91 functional and 6-311+g(d) basis function using Gaussian 09 C.01[1]. Calculation in solution (chloroform) were performed using the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM). The molecular orbitals (MO's) were calculated for each compounds at the optimized geometries (molecules at global minimum – calculated by scanning of dihedral angle C2-C1-C17-O1 in 72 steps 5° each one). The MO's visualization were generated from using Chemcraft version 1.7 (build 365)[2] (Isovalue 0.05). The time-dependent DFT (TD-DFT) studies were performed for singlet excited states (default in Gaussian) for 10 states. The UV-Vis spectra were calculated using the SWizard program, revision 5.0 [3,4] using the Gaussian model.

CRYSTAL09

The single-point periodic calculations were performed in the CRYSTAL09 program. The density functional theory (DFT) method at the B3LYP[5] level with the 6-31+g(d) basis set[6] was applied. The B3LYP level of theory is known to ignore the dispersion energy, therefore, both the Grimme [7,8] dispersion correction and a modified version of the Grimme correction as suggested by Civalleri et. al.[9] was applied. The shrinking factors (IS) along the reciprocal lattice vectors were set at 8. The truncation parameters were set as ITOL1 - ITOL3 = 6, ITOL4 = 7 and ITOL5 = 29. The level shift value was set to 0.6 Hartree. The total energies and periodic wave functions were obtained when the convergence criterion for energy (10^{-7}) was fulfilled.

(S5) X-ray Diffraction study

Structural data and the multipole model for the compound **1a** has been deposited at CSD as CCDC 996918 and is available on request.

A yellow crystal of **1a**, approximate dimensions 0.070 mm x 0.180 mm x 0.220 mm, was used for the X-ray diffraction analysis. The X-ray intensity data were measured on Bruker Kappa Apex-II Ultra four circle diffractometer equipped with molybdenum radiation source (Mo Kα 0.7107 Å, rotating anode). The frames were integrated with the Bruker SAINT[10] software within APEX[11] package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 69918 reflections to a maximum θ angle of 49.79° (0.47 Å resolution), of which 12959 were independent (average redundancy 7.819, completeness = 99.9%, Rint = 4.52%, Rsig = 3.36%) and 42484 (60.76%) were greater than $3\sigma(F^2)$. The final cell constants of $\underline{a}$ =6.9872(2) Å, $\underline{b}$ = 22.0728(8) Å, $\underline{c}$ = 8.3974(3) Å, β = 97.838(2)°, volume = 1283.01(7) Å^3, are based upon the refinement of the XYZ-centroids of 88 reflections above 20 σ(I) with 9.879° < 2θ < 75.69°. Data were corrected for absorption effects using the multi-scan method (SADABS[12]). The ratio of minimum to maximum apparent transmission was 0.940. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9396 and 1.0000. The structure was solved and refined using the SHELXTL Software Package[13] within Olex2[14] graphical environment, with Z = 4 for the formula unit, $C_{20}H_{12}O$. The final anisotropic full-matrix least-squares refinement with spherical scattering factors on F^2 with 202 variables converged at R1 = 4.44%, for the observed data and wR2 = 13.97% for all data. The goodness-of-fit was 1.050. The largest peak in the final difference electron density synthesis was 1.061 e-/Å^3 (in the middle of C18-C19 bond) and the largest hole was -0.266 e-/Å^3 with an RMS deviation of 0.090 e-/Å^3.

The refinement against high-resolution with aspherical scattering factors was performed with XD2006[15][x] package. The Hansen-Coppens formalism[16] was applied, the atomic electron density being divided into three components:

(a) a spherically averaged free-atom Hartree-Fock core contribution, F_{core};
(b) a spherically averaged free-atom Hartree-Fock normalized to one electron valence contribution, $F_{valence}$, with refineable population parameter $P_{valence}$ and the dimensionless expansion-contraction parameter κ;
and (c) a deformation term expressed as normalized Slater-type radial function $R_l(r_k)$ modulated by density normalized, real spherical harmonic angular functions $d_{lm}((\theta,\varphi)$ defined on local axes centered on the atoms and with population parameters P_{lm}, representing the deviation of the valence density from spherical symmetry, modified by the dimensionless expansion-contraction para meter κ_0.

The initial values of the aspherical scattering factors for all atoms but those involved in triple bond (C18, C19) were taken from UBDB aspherical scattering factors databank.[17] Local coordinate systems were assigned according to the UBDB atom types. After initial geometry minimization and refining aspherical scattering density for C18 and C19 atoms, anisotropic

temperature displacement parameters for hydrogen atoms were obtained from SHADE2.1 server,[18] and fixed. Also, the X-H distances were fixed at the distances suggested by UBDB data bank. At the final refinement stage, all multipole parameters were refined together with positional and temperature displacement parameters for all non-hydrogen atoms, and contraction/expansion parameters (κ) for valence electron density for all atoms and additionally κ and κ' parameters for deformation density part for atoms C18 and C19.

The final anisotropic (and in the case of oxygen atom, anharmonic) full-matrix least-squares refinement with aspherical scattering factors on F with 551 variables converged at R1 = 3.05%, for the observed data and wR2 = 3.5% for all data. The goodness-of-fit was 1.557. The largest peak in the final difference electron density synthesis was 0.245 e-/Å^3 and the largest hole was -0.245 e-/Å^3 with an RMS deviation of 0.055 e-/Å^3.

On the basis of the final model, the calculated density was 1.389 g/cm^3 and F(000), 560 e-. The graphics were produced using ORTEP3v2[19] and Mercury3.1[20] programs. Details of data analysis are presented in Table X.

Topological analysis and QTAIM[21] calculations were performed with XDPROP[22] program. The integrated atomic charges summed up for the whole molecule deviate from 0.0e by only 0.002e. The lagrangian values do not exceed 0.001. The difference between the total unit cell volume and the sum of integrated volumes for all atoms within the unit cell is below 2%.

Table 1. Sample and crystal data for 1a.

Chemical formula	$C_{20}H_{12}O$
Formula weight	268.30
Wavelength	0.71070 Å
Crystal size	0.070 x 0.180 x 0.220 mm
Crystal system	monoclinic
Unit cell dimensions	a = 6.9872(2) Å α = 90°
	b = 22.0728(8) Å β = 97.838(2)°
	c = 8.3974(3) Å γ = 90°
Volume	1283.01(7) Å^3
Z	4
Density (calculated)	1.389 g/cm^3
Absorption coefficient	0.084 mm^{-1}
F(000)	560
Theta range for data collection	1.85 to 49.79°
Index ranges	-14<=h<=14, -46<=k<=46, -17<=l<=18
Reflections collected	69919
Independent reflections	12959 [R(int) = 0.0452]
Coverage of independent	99.9%

reflections

Refinement program	SHELXL
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	12959 / 3 / 202
Goodness-of-fit on F^2	1.050
Δ/σ_{max}	0.001
Final R indices	9535 data; I>2σ(I) R1 = 0.0411, wR2 = 0.1206
	all data R1 = 0.0449, wR2 = 0.1266
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0808P)^2+0.3532P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.061 and -0.266 e$Å^{-3}$
R.M.S. deviation from mean	0.090 e$Å^{-3}$
Refinement program	XD2006
Function minimized	$\Sigma\, w(F_o^2- F_c^2)^2$
Data / parameters	9817 / 551
Goodness-of-fit on F^2	1.557
Δ/σ_{max}	0.000
Final R indices	9817 data; I>2σ(I) R1 = 0.0305, wR2 = 0.0250
	all data R1 = 0.0650, wR2 = 0.0350
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0P)^2+0.0P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.245 and -0.245 e$Å^{-3}$
R.M.S. deviation from mean	0.055 e$Å^{-3}$
DMSDA max [$1.E^4\ Å^2$]	5 / C18 – C19

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