RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

Synthesis and Solid-state Fluorescence Properties of Pentacyclic 7-Substituted-indeno[1',2':4,5]pyrido[2,1-*a*]isoindol-5-ones†

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

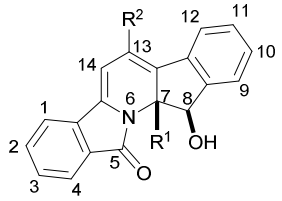
Z.Chamas,[a] E.Marchi,[b] B.Presson,[a] E.Aubert,[c] Y.Fort,[a] P.Ceroni,[b,]* and V.Mamane,[a,d,]*

With the aim to design fluorescent solids, a series of indeno[1',2':4,5]pyrido[2,1-a]isoindol-5-ones with various substituents was prepared. In these π-extended pentacyclic derivatives, the presence of a methyl group in 7-position was found to have a critical influence on the fluorescence properties in the solid state. Crystal packing of the non-substitutedderivatives shows strong π-π interactions causing quenching of the fluorescence. In contrast, by introducing a methyl substituent in 7-position we obtained compounds with fluorescence quantum yield up to 32% in the solid state.

Introduction

Solid-state organic luminescent compounds[1,2] have received considerable attention for practical use in organic electroluminescence devices (OLED),[3] solid-state dye laser[4] and sensors.[5] Only a few compounds exhibit strong fluorescence both in solution and in the solid state because most of them undergo fluorescence quenching in aggregation state. Indeed, strong intermolecular interactions between neighbouring fluorophores generally lead to fluorescence quenching in the solid state.[6]

We have recently described the synthesis of N-containing pentacyclic compounds via a cascade reaction between 2,5-dihalopyridines and 2-formylbenzeneboronic acids.[7] Most of the compounds exhibited excellent fluorescence properties in solution,[8]but not in the solid state. However, compounds **1** and **2** bearing a methyl group in 7-position (Figure 1) were identified as fluorescent solids. Introduction of a methyl substituent in 7-position could prevent strong intermolecular packing through π•••π interactions in the solid state thus avoiding quenching of the fluorescence.In the non-substituted pentacycles (for instance **3** and **4**), the fluorescence is quenched as a result of strong π•••π stacking interactions in such extended π-conjugated systems.[7] Based on these preliminary observations, we report herein the preparation and the photophysical study of new derivatives bearing a methyl or aryl substituent in 7-position. The fluorescence measurements confirm that all compounds with a methyl group in 7-position possess high quantum yields of fluorescence in the solid state whereas they are low in case of the aryl substituted compounds.The crystal structures of selected compounds were analysed in order to investigate the influence of the crystal packing on the fluorescence properties.



R^1 = Me, R^2 = H **1**
R^1 = R^2 = Me **2**
R^1 = R^2 = H **3**
R^1 = H, R^2 = Me **4**

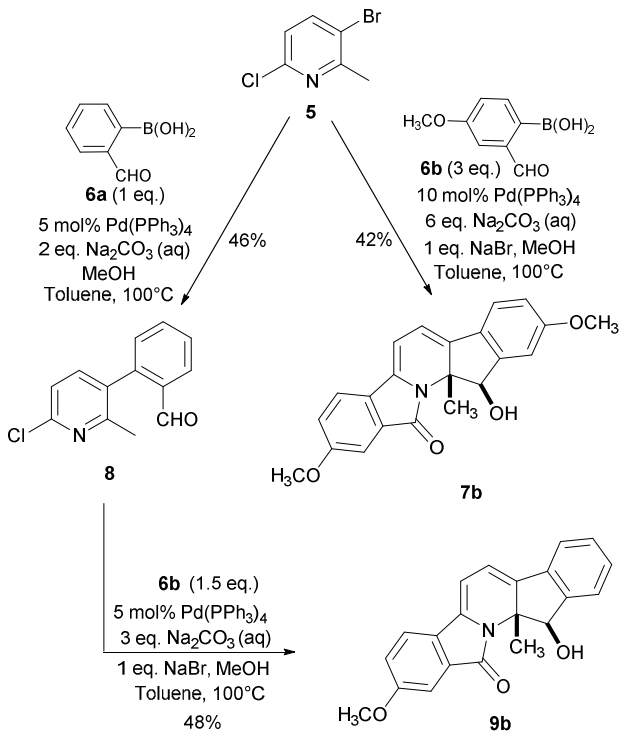
Fig. 1 Fluorescent pentacyclic compounds

Results and discussion

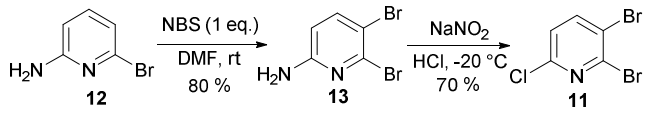
Synthesis

Pentacyclic compounds bearing an electron-donating substituent (OCH_3) were prepared starting from pyridine **5** (Scheme 1). The cascade reaction of **5** with 3 eq. of boronic acid **6b** yielded **7b**. Alternatively, the reaction of **5** with one eq. of 2-formylbenzeneboronic acid **6a** furnished intermediate **8** in moderate yield along with pentacycle**3** which formation was initiated *in situ* by a competitive second Suzuki coupling. Next, the reaction of **8** with 1.5 eq. of **6b** gave pentacycle**9b** having one methoxy substituent. Compounds **7b** and **9b** represent the analogues with a methyl substituent in 7-position of **7a** and **9a**, respectively (see Figure 2for the structures of **7a** and **9a**).

In order to extend the family of 7-substituted pentacycles, it was necessary to access to new 2-chloro-5-bromo-pyridines (Scheme 3) bearing a substituent in 6-position. For this purpose, the trihalopyridine substrate **11** was chosen as the key compound since it could allow a selective cross-coupling in 6-position. Pyridine **11** was prepared from 2-amino-6-bromo-pyridine **12** in two steps with an overall good yield.



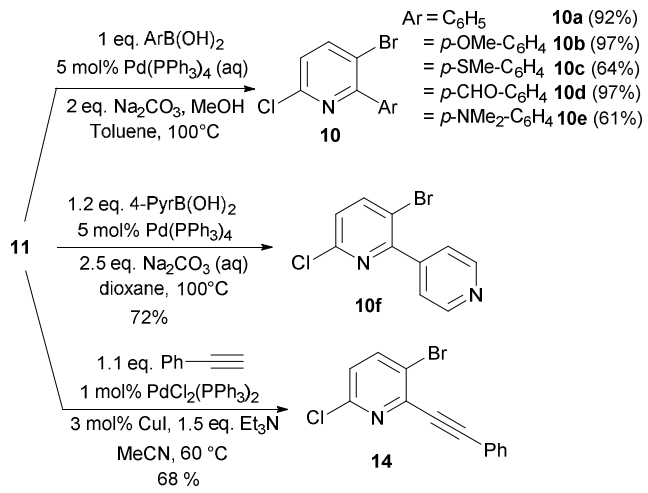
Scheme 1 Synthesis of pentacycles**7b** and **9b**



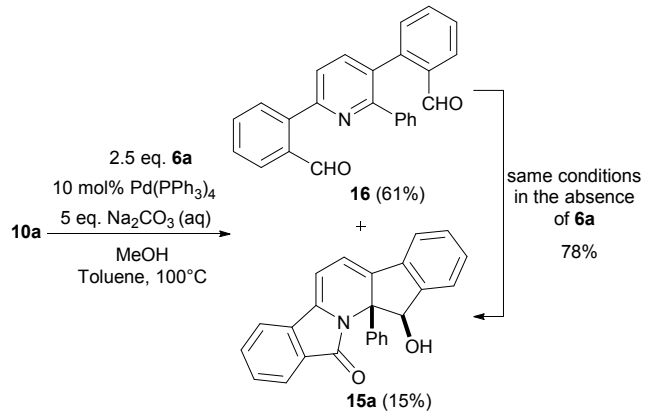
Scheme 2 Synthesis of trihalopyridine**11**

Electrophilic bromination of **12** furnished the dibromoaminopyridine**13**,[9] followed by the replacement of the amino group by a chlorine through a Sandmeyer-type reaction to give **11** (Scheme 2).The cross-coupling of **11** in 6-position was performed with 1 eq. of various boronic acids to deliver the expected 2-chloro-5-bromo-6-arylpyridines **10a-e** in good yields. Little change of the procedure allowed obtaining the pyridine-substituted derivative **10f** in good yield. The Sonogashira coupling of **11** with a slight excess of phenylacetylene performed also smoothly to give **14** in good yield (Scheme 3).

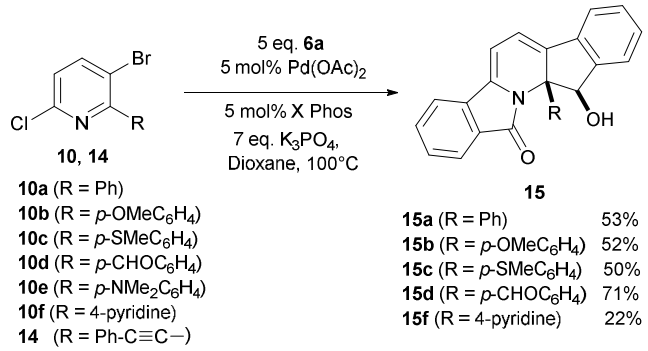
Pyridine **10a** was then reacted with 2.5 eq. of 2-formylphenylboronic acid **6a** under standard conditions to give the expected pentacycle**15a** in low yield and a large amount of non-cyclized bis-aldehyde **16**. Obviously the presence of the bulky phenyl group reduced the pyridine nitrogen reactivity toward the aldehyde[10,11] thus increasing the stability of **16**.[12]Moreover, when bis-aldehyde **16** was subjected to the same reaction conditions, pentacycle**15a** was formed in good yield. When the catalyst was omitted the pentacycle was still formed althoughin a lower yieldof 20% because of theimportantformation of degradation products (Scheme 4).



Scheme 3 Synthesis of 6-substituted 2-chloro-5-bromopyridines



Scheme 4 Synthesis of pentacycle**15a** under standard conditions



Scheme 5 Cascade reaction of 6-substituted pyridines **10** and **14**.

Nevertheless, these experiments suggest that a more robust palladium catalyst could allow performing the cascade reaction in a single step. The bulky monophosphine ligand such as XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) has shown high performances in Suzuki coupling[13] and other palladium-catalyzed reactions.[14] The cascade reaction was then performed with catalytic system [$Pd(OAc)_2$, XPhos] and it was noticed that 5 equivalents of 2-formylphenylboronic acid **6a** were needed for the reaction to go to completion (Scheme 5).

Under these conditions, the yield for pentacycle**15a** could be increased to 53%. Pyridines **10b-d** reacted smoothly to give compounds **15b-d** in good yields whereas a moderate yield for **15f** was obtained with bipyridine**10f**. Complex mixtures were obtained after the reaction of substrates **10e** and **14**. As for pentacycle**1**,[7] the relative *syn* configuration was confirmed for compounds**2**,**15a** and **15d** by XRD and was applied to the other compounds of the series **15b-c** and **15f** (vide infra).

To summarize, the structures of all the compounds considered in this study are depicted in Figure 2.

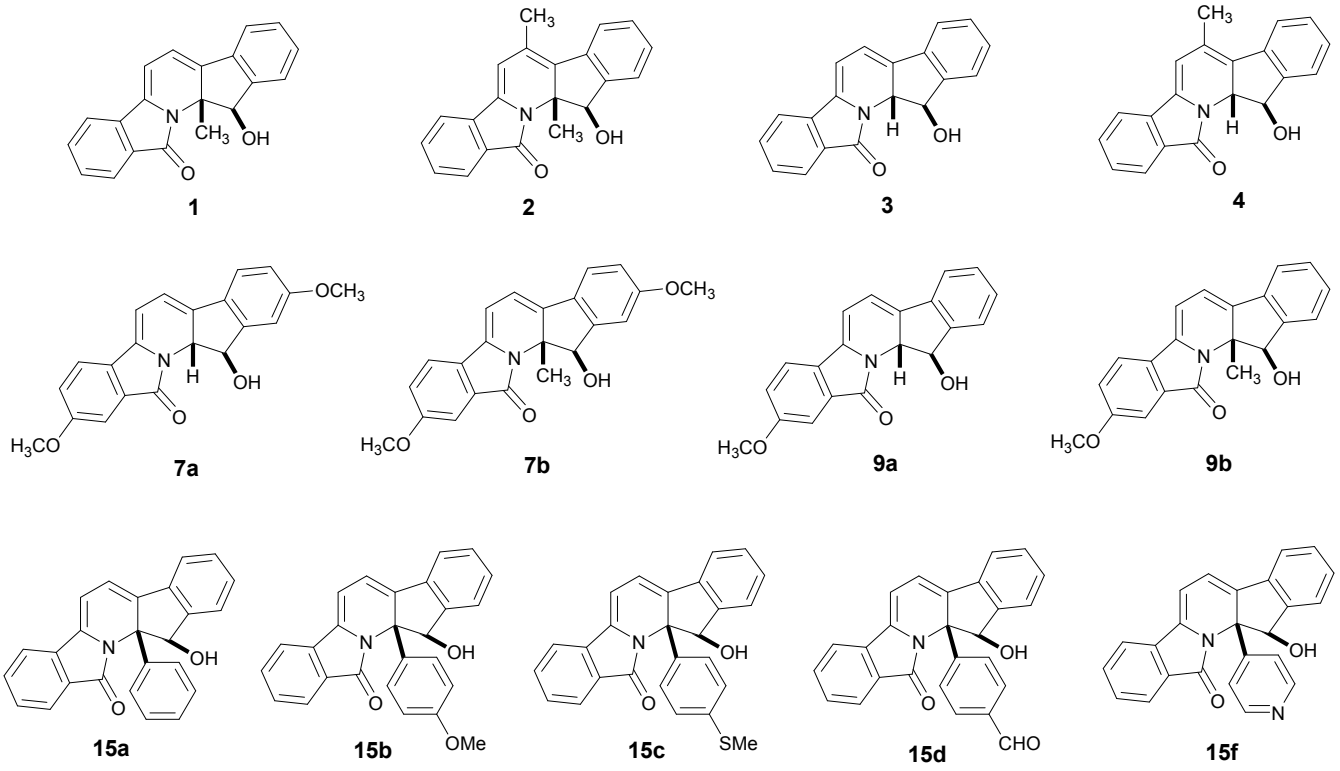


Fig. 2 Overview of the pentacyclic compounds

Photophysical properties

In CH_2Cl_2 solution. The photophysical properties of compounds **1-4** are very similar: as an example, the absorption and emission spectra of **2** are reported as solid black lines in Figure 3 and 4, respectively. Compounds **1-4** display the same lowest-energy absorption band, a bright emission at ca. 500 nm, with an intensity decay of few ns, insensitive to the presence of dioxygen in solution (Table 1), thus pointing to a fluorescent excited state. These results demonstrate that the presence of the methyl substituents in position 7 and/or 13 does not significantly affect the optical properties in solution.

Upon appending one (**9b**) or two methoxy units (**7b**) at the external phenyl rings, a new band at ca. 330 nm arises in the absorption spectra and it can be attributed to electronic transitions of the methoxybenzene units. The emission spectrum of **9b** is similar to the previously discussed spectrum of **2** (Figure 3) with a remarkably high emission quantum yield (Table 1). On the other hand, compound **7b** displays a weak emission band with no vibronic structure, a red-shifted maximum and a shorter lifetime. The photophysical properties of compounds **7b** and **9b** are very similar, in terms of energy, lifetime and emission quantum yield, to the corresponding previously investigated analogues **7a** and **9a**lacking the methyl substituent in position 7 (Figure 2).[8] This experimental finding points to the fact that the methyl substituent in that position does not affect the electronic properties of the chromophores in solution.

Compounds **15a-d** and **15f** have the same photophysical properties and the absorption (Figure 3) and emission spectra (Figure 4) of compound **15a**, reported as a representative example, are very similar also from a quantitative point of view (Table 1) to those of compound **1**.

In solid state. As previously discussed, highly luminescent organic molecules in solution are often not emissive in the solid state. We thus decided to investigate the emission spectra and the emission quantum yield in the solid state of all the above reported compounds. Compounds **3** and **4**, as well as compounds **15a-d** and **15f**, which are all strongly emissive in CH_2Cl_2 solution, are either completely quenched or poorly emissive as a powder (Table 1). On the contrary, compounds **1**, **2**, **7b** and **9b** display a strong emission (Φ_{em} ca. 30%) in the solid state. The emission spectra in the solid state of two representative examples (**1** and **15a**) are reported in Figure 5.

Table 1. Most relevant photophysical data for all the compounds in air-equilibrated CH_2Cl_2 solution and in solid state at 298 K.

	Absorption		Emission[a]				
	CH_2Cl_2		CH_2Cl_2			Solid	
	λ (nm)	ε ($M^{-1}cm^{-1}$)	λ_{max} (nm)	τ (ns)	Φ_{em}[a]	λ (nm)	Φ_{em}
1	421	22000	500	4.60	0.67	520	0.31
2	425	17000	512	5.27	0.77	531	0.29
3	423	18000	497	4.30	0.62	-[b]	-[b]
4	424	-[c]	505	-[c]	0.71	-[b]	-[b]
7a	430	180000	518	0.7	0.11	-[d]	-[d]
7b	432	20000	523	0.47	0.07	549	0.32
9a	422	170000	498	5.10	0.78	-[d]	-[d]
9b	423	21000	501	5.05	0.79	544	0.21
15a	423	16700	502	4.88	0.74	552	0.09
15b	422	16200	502	4.60	0.67	569	0.06
15c	421	16700	501	4.79	0.62	586	0.08
15d	422	16500	503	5.27	0.77	517	0.07
15f	421	17900	501	5.33	0.73	557	0.06

[a]Fluorescence quantum yields in solution were measured using as standard perylene in air equilibrated EtOH solution (Φ_{em} = 0.92) and in solid state by an integrating sphere (see Experimental section). [b]No emission detected in the solid state. [c] These data are not reported because the sample is not fully stable in solution. [d]Data not available.

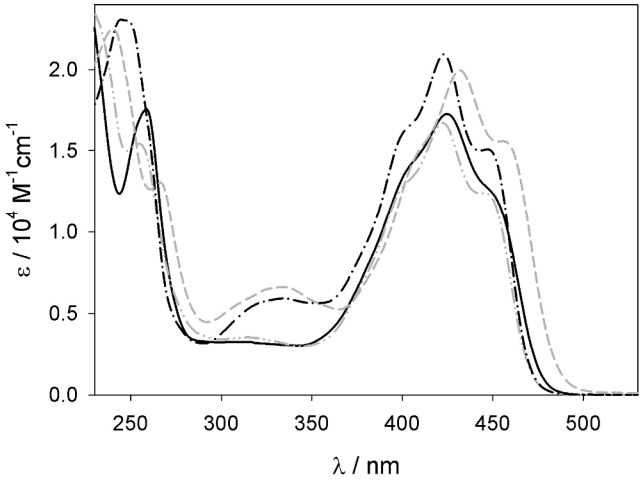


Fig. 3 Absorption spectra of compounds **2** (solid black line), **7b** (dashed gray line), **9b** (dashed dotted black line) and **15a** (dashed dotted dottedgray line) in CH_2Cl_2 solution.

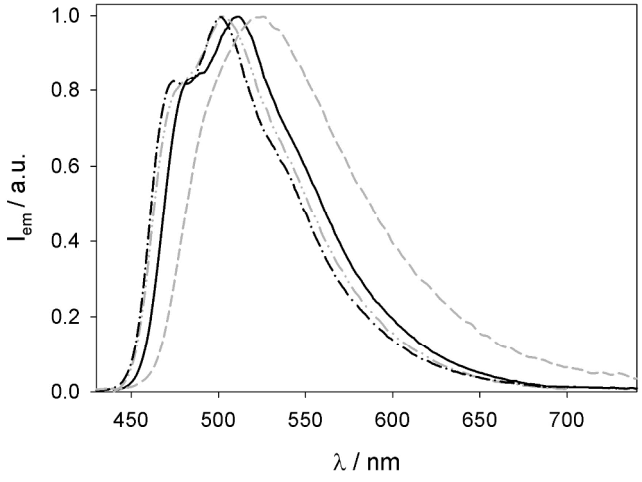


Fig. 4 Normalized emission spectra of compounds **2** (solid black line), **7b** (dashed gray line), **9b** (dashed dotted black line) and **15a** (dashed dotted dottedgray line) in CH_2Cl_2 solution. λ_{ex} = 400 nm.

It is worth noting that compound **7b** is poorly emissive in solution. Indeed, based on the previous investigation,[8] for the lower emitting compounds the fluorescent excited state is mainly deactivated by non radiative pathways which are strongly inhibited in rigid environment (as in the solid state or in film): this may explain the strong increase of emission quantum yield in the case of **7b**.

The discussed emission properties in the solid state are not a function of the degree of crystallinity, as demonstrated by comparing the emission quantum yields measured for powder samples and drop-cast solutions on glass slides.

To sum up these results, we can conclude that: (i) compounds with a methyl substituent in position 7 are the most emissive in solid, (ii) lower emission intensities are displayed by the phenyl substituted compounds, (iii) while compounds **3** and **4** bearing no substituent are not emissive. Therefore, the presence of a methyl or phenyl substituent in position 7 does strongly affect the emissive properties in the solid state, but not in solution (see above).

X-ray Diffraction Analysis

Crystal structures were determined by single crystal X-ray diffraction for compounds **2**, **15a** and **15d**; the structures of **1**,**4** and**7a** were published in a previous article.[7] In all investigated structures, the OH and R^1 group in 7-position are in *syn* conformation. Moreover, in **15a** and **15d**the same molecular synthons formed by O,C—H•••O hydrogen bonding are observed (Figure 6). These synthons are built from four molecules around an inversion center in **15a**, and about a

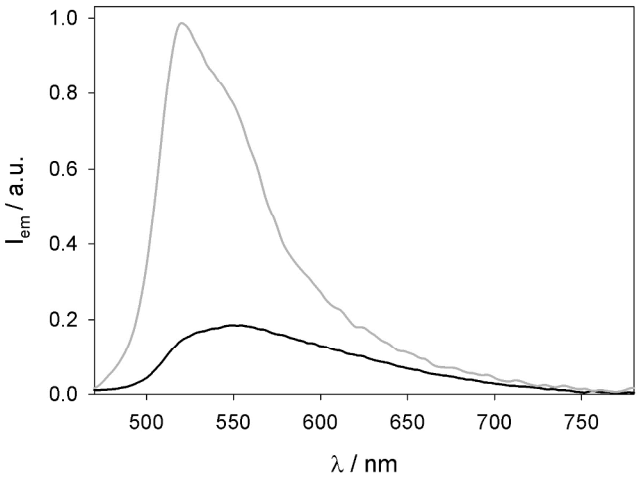


Fig. 5 Emission spectra of compounds **1** (gray line) and **15a** (black line) as a powder.λ_{ex} = 400 nm. These spectra are not corrected for the reabsorption of the emitted light.

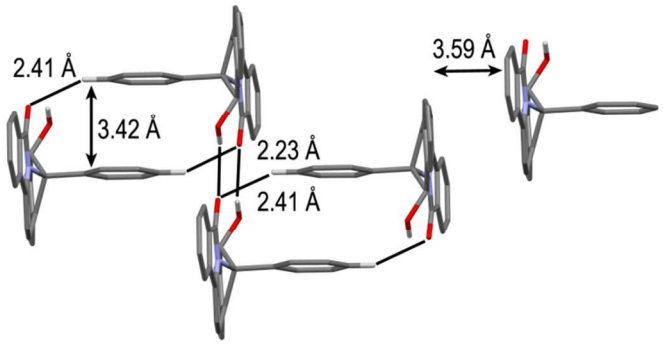


Fig.6 Molecular synthon about inversion center(left part of the figure)formed by O,C—H•••O hydrogen bonds and π•••π interactions (displayed as black lines) in **15a**. Hydrogen atoms not involved in intermolecular bonding are omitted for clarity.

pseudo inversion center in the non-centrosymmetric structure of **15d**; in this latter structure, the loss of inversion symmetry is induced by the ordering of the dichloromethane solvent molecules that are cocrystallised together with the pentacyclic compound. A similar molecular arrangement was also found in 3,10-dimethoxy related pentacycle**7a** but not in **4** and **1-2**.[7] The molecular packing in **15a** presents π•••π interactions involving the pentacyclic backbone by its concave side (3.59Å) and the phenyl group in 7-position (3.42Å) separately.

On the contrary, in **15d** π•••π interactions couple together *p*-CHO-C_6H_4 groups and pentacyclic backbones by their concave side (3.67Å).

These packing are noticeably different from the one displayed by other related compounds. In the case of **4**, the presence of the H atom in 7-position induces strong molecular packing through C—H•••N hydrogen bond (H•••N=2.55Å; C—H•••N=164.9°) and π•••π interactions (3.67Å) involving the whole pentacyclic backbone, through its concave and convex sides (Figure 7a). The molecular packing is also different in the

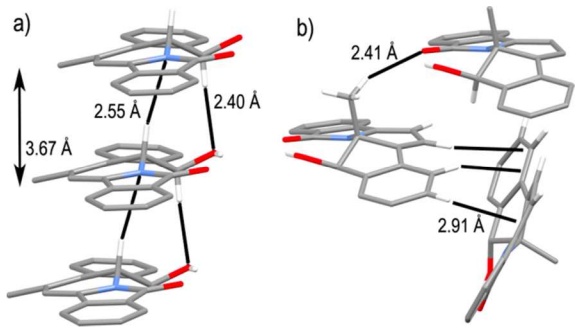


Fig.7 Molecular packing of a)**4**, showing the strong π•••π interaction involving the whole pentacylic backbone together with the C—H•••N,O hydrogen bond (displayed as black lines) and of b) **1** Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

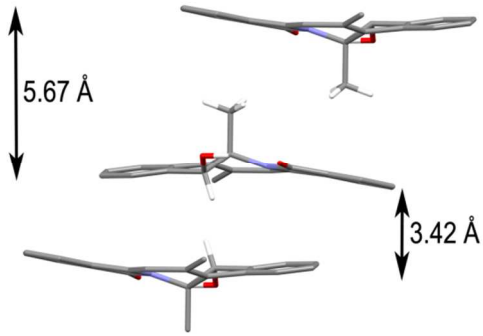


Fig.8 Molecular packing of **2**, showing the π•••π interaction involving the concave side of the pentacycle; the methyl group precludes such interaction from the convex side of the molecule.

case of **1** where it is driven by multiple C—H•••O,π hydrogen bonds and contacts with no π•••π interactions (Figure 7b). As what is observed for **15a**, **2** presents π•••π interactions involving the pentacyclic backbone by it concave side (3.42Å) but cannot display the additional stacking interactions observed in **15a** due to the non-aromatic nature of the R^1 (methyl) group (Figure 8).

Correlating these structural features to the photophysical properties shows that intermolecular π•••π interactions are detrimental to fluorescence in the solid state. Indeed, with strong π•••π overlap as in **4**involving both side of the molecule, no fluorescence is observed in the solid state despite of a good quantum yield in solution, while a small solid state quantum yield is obtained when this overlap is reduced (**15a** and **15d**). In these last compounds, hydrogen bonding can also participate to the fluorescence quenching by bringing the molecules in close proximity one to each other. The highest yield is obtained for the crystal structure displaying no π•••π interactions (**1**) or with only the concave side of the molecule (**2**), where the quantum yield is only halved going from solution to solid state.

Conclusions

We have succeeded in designing fluorescent solids by slight structural modification of the pentacyclic framework of indeno[1',2':4,5]pyrido[2,1-*a*]isoindol-5-ones. Indeed, the

original pentacyclic compounds exhibitedhigh fluorescence in solution but led to non-fluorescent solids due to π-π interactions which maintained the molecules in close proximity thus leading to fluorescence quenching. The introduction of a methyl group on the central pyridine ring close to the nitrogen (7-position) induced weaker π-π interactions and increased fluorescence in the solid state. Aryl groups on the same 7-position did not have the same improving effect on the solid state fluorescence due to additional π-π interactions between the added aryl groups.

Experimental

General remarks

Toluene and dioxane were distilled over sodium/benzophenone and stored over sodium. All other solvents and reagents were used as received. TLC was performed on silica gel plates and visualized with a UV lamp (254 nm). Chromatography was performed on silica gel (70-230 mesh). Melting points were measured on a Totoli apparatus. Proton and carbon NMR spectra were recorded on Bruker AC-200, AC-250 or AM-400 Fourier transform spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane. Coupling constants J are quoted in Hz. Mass spectra with electronic impact (MS-EI) were recorded from a Shimadzu QP 2010 apparatus. High resolution mass spectra were recorded from a BruckermicrOTOFQ (APCI-TOF).

Photophysical measurements

UV-Vis absorption spectra were recorded in solution with quartz cuvettes (optical pathlength 1 cm and 5 cm, Hellma®) by using a Perkin Elmer λ650 spectrophotometer. Corrected fluorescence emissions, excitation spectra and emission lifetimes were recorded in solution with an Edinburgh FLS920 spectrofluorimeter equipped with Hamamatsu H5773-04 phototube and a TCC900 card for data acquisition in time-correlated single-photon counting experiments (22 ps time resolution) by using a continuous 450 W Xenon arc lamp or a PicoQuant LDH-P-C-405 pulsed diode laser as excitation source. Fluorescence quantum yields were measured following the method of Demas and Crosby[15] (standard used: perylene in air equilibrated EtOH solution, Φem = 0.92).[16] Solid emission spectra and solid emission quantum yields were measured by an Edinburgh FLS920 spectrofluorimeter equipped with a barium sulfate coated integrating sphere (LabSphere, 4P-GPS-040-SF), a continuous 450 W Xenon arc lamp as light source and a Hamamatsu H5773-04 phototube, following the procedure described by De Mello *et al.*.[17] The experimental errors are within: ±2 nm of the band maximum, 5% of the molar absorption coefficient, 10% of the lifetime measurements, and 15% of the emission quantum yield in solid.

Single Crystal X-ray Diffraction

Single crystals were obtained by slow evaporation from dichloromethane solutions. Diffraction experiments were performed on a SuperNova CCD diffractometer (Agilent Technologies) using the CuKα radiation (λ=1.5418Å) for **2**, **15a** and **15d**. Data collections under dinitrogen stream were obtained at 100K for **15a** and 110K for **2** and**15d**, respectively. The structures were solved by direct methods with the program SIR-92[18] and full matrix least-square refinements on F2 in SHELX-97[19] were performed with anisotropic displacements for non-H atoms. Hydrogen atoms were located in difference Fourier maps and refined isotropically according to the riding model.

3,10-Dimethoxy-7,8-dihydro-8-hydroxy-7-methyl-indeno[1',2':4,5]pyrido[2,1-a]isoindol-5-one (7b)

To a degassed toluene solution (12 mL) containing $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) and pyridine **5** (206.5 mg, 1 mmol), degassed solution of boronic acid **6b** (3 mmol) in methanol (3 mL) and aqueous solution (4 mL) of Na_2CO_3 (636 mg, 6 mmol) and NaBr (103 mg, 1 mmol) were successively added. After heating for 12h at 100°C, the reaction mixture was cooled to room temperature, extracted with ethyl acetate (3 x 20 mL) and dried over anhydrous magnesium sulphate ($MgSO_4$). After filtration on Celite and concentration, the residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate) to give compound **7b** (150 mg, 42%); mp 152–154°C; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 7.58 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 2.3 Hz, 1H), 7.10–7.17 (m, 2H), 6.89 (ddd, *J* = 8.4, 2.3, 0.6 Hz, 1H), 6.37 (d, *J* = 6.3 Hz, 1H), 6.19 (d, *J* = 6.3 Hz, 1H), 5.51 (s, 1H, OH), 5.34 (d, *J* = 0.6 Hz, 1H), 3.89 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 1.25 ppm (s, 3H, CH_3); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 169.7, 161.3, 160.8, 145.4, 141.8, 132.3, 129.6, 128.4, 128.35, 122.5, 121.4, 120.6, 116.6, 110.2, 108.6, 105.6, 103.0, 79.7, 67.7, 55.8, 55.6, 17.5 ppm. HRMS *m/z*calcd for $C_{22}H_{19}NNaO_4$ (M + Na): 384.1206, found: 384.1206.

2-(6-Chloro-2-methyl-pyridin-3-yl)-benzaldehyde (8)

To a degassed toluene solution (15 mL) containing $Pd(PPh_3)_4$ (173 mg, 0.15 mmol) and pyridine **5** (620 mg, 3 mmol) were successively added degassed solutions of 2-formylbenzeneboronic acid **6a** (450 mg, 3 mmol) in methanol (6 mL) and Na_2CO_3 (636 mg, 6 mmol) in water (6 mL). After heating for 12h at 100°C, the reaction mixture was cooled to room temperature, extracted with ethyl acetate and dried over $MgSO_4$. After concentration, the residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate) to give **8** (320 mg, 46%). Mp 88–90°C; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 9.81 (s, 1H, CHO), 8.04 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.70 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.59 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.31 ppm (s, 3H, CH_3); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 190.9, 157.2, 150.2, 141.2, 140.0, 134.1, 133.7, 132.0, 130.7, 129.0, 128.8, 121.2, 22.9 ppm. MS (70 eV): *m/z* (%) 231 (M^+, 100), 216 (58), 202 (33), 166 (33); HRMS *m/z*calcd for $C_{13}H_{11}ClNO$ (M + H): 232.0524, found: 232.0532.

3-Methoxy-7,8-dihydro-8-hydroxy-7-methyl-indeno[1',2':4,5]pyrido[2,1-a]isoindol-5-one (9b)

To a degassed toluene solution (2 mL) containing $Pd(PPh_3)_4$ (25 mg, 0.022 mmol) and pyridine **8** (50 mg, 0.216mmol) were successively added degassed solution of boronic acid **6b** (58 mg, 0.324mmol) in methanol (1 mL) and aqueous solution (1 mL) of Na_2CO_3 (69 mg, 0.648 mmol) and NaBr (22.3 mg, 0.216 mmol). After heating for 12h at 100°C, the reaction mixture was cooled to room temperature, extracted with ethyl acetate and dried over $MgSO_4$. After concentration, the residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate) to give **9b** (34 mg, 48%). Mp 132–134°C; ^{1}HNMR ($CDCl_3$, 400 MHz) δ 7.61 (d, *J* = 6.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 6.4 Hz, 1H), 7.37 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.33 (t, *J* = 6.4 HZ, 1H), 7.30 (d, *J* = 2.0 Hz,

1H), 7.14 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.50 (d, *J* = 6.2 Hz, 1H), 6.18 (d, *J* = 6.2 Hz, 1H), 5.55 (br s, 1H, OH), 5.23 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H, OCH_3), 1.25 (s, 3H, CH_3); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 169.7, 161.0, 143.2, 141.8, 135.8, 133.4, 129.8, 129.4, 128.5, 128.2, 125.0, 121.6, 121.1, 120.6, 112.4, 105.8, 102.4, 79.8, 67.6, 55.8, 17.4 ppm. HRMS *m/z*calcd for $C_{21}H_{17}NNaO_3$ (M + Na): 354.1111, found: 354.1101.

2-Amino-5,6-bromopyridine(13)

To a solution of 6-amino-2-bromopyridine **12** (3.46 g, 20 mmol) in DMF (100 mL) was added NBS (3.56 g, 20 mmol). The solution was stirred at room temperature for 6h. The progress of the reaction was monitored by TLC. After disappearance of starting material, themixture was poured into 200 mL of cold water. The product precipitated immediately. After filtration and drying, **13**was obtained as a white powder (4 g, 80%). Mp 149–151°C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.65 (s, 2H, NH_2), 6.37 (d, *J* = 8.5 Hz, 2H), 7.56 ppm (d, *J* = 8.5 Hz, 1H); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 156.7, 142.6, 140.9, 109.5, 108.6 ppm. MS (70 eV): *m/z* (%) 252 (M^+, 100), 171 (42), 92 (65), 64 (40), 41 (42); HRMS *m/z*calcd for $C_5H_5Br_2N_2$: 250.8814 (M + H), found: 250.8810.

2,3-Dibromo-6-chloropyridine (11)

To a solution of 2-amino-5,6-bromopyridine **13** (3.65 g, 14.5 mmol) in conc. HCl (35 mL) at -20°C was added $NaNO_2$ (2 g, 29 mmol) slowly by small portions and the mixture was stirred at room temperature for 4h. NaOH 10M was added until pH11 and the product was extracted with ethyl acetate (3 x 150 mL). The organic phase was washed with brine (100 mL) and dried over $MgSO_4$ and concentrated. The crude was purified by chromatography on silica gel (cyclohexane / ethyl acetate 4/1) to give **11** as a white powder (2.73 g, 70%). Mp 67–69°C; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.18 ppm (d, *J* = 8.0 Hz, 1H); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 148.8, 143.5, 142.4, 124.3, 122.4 ppm. MS (70 eV): *m/z* (%) 271 (M^+, 85), 192 (72), 110 (50), 75 (100), 50 (76); HRMS *m/z*calcd for $C_5H_3Br_2ClN$: 269.8315 (M + H), found: 269.8305.

General procedure for the preparation of 3-bromo-6-chloro-2-arylpyridine(10)

To a degassed toluene solution (4 mL) containing $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and **11** (269 mg, 1 mmol) were successively added degassed solutions of the corresponding boronic acid (1 mmol) in methanol (2 mL) and Na_2CO_3 (212 mg, 2 mmol) in water (2 mL). After heating for 6h at 100°C, the reaction mixture was cooled to room temperature, extracted with ethyl acetate and dried over $MgSO_4$. After concentration, the residue was purified by chromatography on silica gel (cyclohexane / ethyl acetate) to give the desired compounds.

3-Bromo-6-chloro-2-phenylpyridine(10a)

Yield: 92% (247 mg); mp 104–106°C; ^{1}HNMR ($CDCl_3$, 250 MHz) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.75–7.65 (m, 2H), 7.50–7.40 (m, 3H), 7.16 ppm (d, *J* = 8.4 Hz, 1H); ^{13}CNMR ($CDCl_3$, 62.5 MHz) δ 158.3, 149.6, 143.7, 138.1, 129.3, 129.2, 128.0, 123.8, 117.8 ppm. MS (70 eV): *m/z* (%) 269 (M^+, 35), 188 (100), 153 (50), 76 (40), 50 (35); HRMS *m/z*calcd for $C_{11}H_8BrClN$ (M + H): 267.9523, found: 267.9531.

3-Bromo-6-chloro-2-(4-methoxyphenyl)pyridine(10b)

Yield: 97% (289 mg); mp 93–95°C; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 3.87 ppm (s, 3H, OCH_3); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 160.3, 157.7, 149.5, 143.7, 130.9, 130.5, 123.2, 117.5, 113.3, 55.2 ppm. MS (70 eV): *m/z* (%) 299 (M^+, 100), 218 (95), 175 (40), 140 (75), 113 (45), 63 (55); HRMS *m/z*calcd for $C_{12}H_{10}BrClNO$ (M + H): 297.9629, found: 297.9640.

3-Bromo-6-chloro-2-(4-(methylthio)phenyl)pyridine (10c)

Yield: 64% (201 mg); mp 116–118°C; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7. 31 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 2.52 ppm (s, 3H, SCH_3); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 157.5, 149.6, 143.7, 140.4, 134.4, 129.7, 125.3, 123.6, 117.6, 15.2 ppm. MS (70 eV): *m/z* (%) 315 (M^+, 100), 219 (18), 140 (20); HRMS *m/z*calcd for $C_{12}H_{10}BrClNS$ (M + H): 313.9400, found: 313.9386.

4-(3-Bromo-6-chloropyridin-2-yl)benzaldehyde (10d)

Yield: 97% (287 mg); mp 143–145°C; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 10.10 (s, 1H, CHO), 8.01-7.96 (m, 3H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.24 ppm (d, *J* = 8.5 Hz, 1H); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 191.8, 157.0, 150.0, 143.9, 143.7, 136.5, 130.2, 129.4, 124.7, 117.9 ppm. MS (70 eV): *m/z* (%) 297 (M^+, 100), 266 (20), 216 (100), 187 (25), 152 (52), 125 (32), 75 (47), 50 (60); HRMS *m/z*calcd for $C_{12}H_8BrClNO$ (M + H): 295.9472, found: 295.9476.

3-Bromo-6-chloro-2-[4-(dimethylamino)phenyl]pyridine (10e)

Yield: 61% (190 mg); ^{1}HNMR ($CDCl_3$, 200 MHz) δ 3.03 (s, 6H, $N(CH_3)_2$), 6.77 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.85 ppm (d, *J* = 8.3 Hz, 1H); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 40.1, 111.0, 117.0, 122.2, 125.5, 130.56, 143.7, 149.3, 150.8, 158.0 ppm. MS (70 eV): *m/z* (%) 312 (M^+, 100), 195 (26), 152 (22), 42 (30); HRMS *m/z*calcd for$C_{13}H_{13}BrClNO$ (M + H): 310.9945,found: 310.9948.

4-(3-Bromo-6-chloropyridin-2-yl)pyridine (10f)

Pyridine **11** (272 mg, 1 mmol), 4-pyridine boronic acid (85% purity, 174 mg, 1.41 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05mmol) were placed in a Schlenk tube under argon. Degassed dioxane (7 mL) and a degassed solution of aqueous Na_2CO_3 (1 M, 3 mL, 3 mmol) were added and the mixture was heated under reflux for 18h. After heating cooling to room temperature, the mixture was extracted with ethyl acetate and dried over $MgSO_4$. After concentration, the residue was purified by chromatography on silica gel (cyclohexane / ethyl acetate 4/1) to give pyridine **10f** as a white powder (150 mg, 56%). Mp 115–117°C; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 8.75 (s, 2H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 4.0 Hz, 2H), 7.25 ppm (d, *J* = 8.5 Hz, 1H); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 155.5, 150.1, 149.7, 145.4, 144.0, 125.1, 123.7, 117.7 ppm. MS (70 eV): *m/z* (%) 270 (M^+, 44), 189 (100), 162 (30), 127 (24); HRMS *m/z*calcd for $C_{10}H_7BrClN_2$ (M + H): 268.9476, found: 268.9484.

3-Bromo-6-chloro-2-(phenylethynyl)pyridine(14)

An oven-dried resealable tube was charged with **11**(269 mg, 1 mmol), CuI (5 mg, 0.03 mmol) and $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) then placed under argon. Degassed acetonitrile (1.5 mL) and triethylamine (0.2 mL, 1.5 mmol) were added. Finally, phenylacetylene (112.3 mg, 1.1 mmol) was added and the

mixture was heated at 60°C for 12h. After cooling, the mixture was extracted with ethyl acetate (3x15 mL), dried and concentrated. The residue was purified by chromatography on silica gel (cyclohexane / ethyl acetate 3/1) to give **14** as a white product (200 mg, 68%). Mp 148–150°C; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 7.15 (d, *J* = 8.4 Hz, 1H), 7.37-7.41 (m, 3H), 7.62-7.67 (m, 2H), 7.85 ppm (d, *J* = 8.4 Hz, 1H). ^{13}CNMR ($CDCl_3$, 50 MHz) δ 149.6, 143.4, 142.1, 132.2, 129.6, 128.4, 124.4, 122.1, 121.4, 95.4, 86.5 ppm. MS (70 eV): *m/z* (%) 252 ([M – C_3H_3]$^+$, 99], 171 (45), 92 (83), 64 (100), 41 (86); HRMS *m/z*calcd for $C_{13}H_8BrClN$ (M + H): 291.9523, found: 291.9503.

Cascade reaction of 10a under standard conditions. Formation of 16 and 15a

To a degassed toluene solution (7.5 mL) containing $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and pyridine **10a** (134 mg, 0.5 mmol), degassed solutions of 2-formylbenzeneboronic acid **6a** (186 mg, 1.25 mmol) in methanol (1.25 mL) and Na_2CO_3 (265 mg, 2.5 mmol) in water (2.5 mL) were successively added. After heating for 12h at 100°C, the reaction mixture was cooled to room temperature, extracted with ethyl acetate (3 x 20 mL) and dried over anhydrous $MgSO_4$. After filtration on Celite and concentration, the residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate 9/1) to give **16** (90 mg, 61%) and **15a** (30 mg, 15%).

2-[2-(6-Phenyl-pyridin-2-yl)-benzaldehyde]-benzaldehyde (16)

^{1}HNMR ($CDCl_3$, 200 MHz) δ 10.35 (s, 1H, CHO), 9.84 (s, 1H, CHO), 8.05 (d, *J* = 7.4 Hz, 1H), 8.00–7.00 ppm (m, 14H). MS (70 eV): *m/z* (%) 363 (M$^+$, 80), 286 (100), 258 (30), 202 (30), 77 (80), 51 (65).

7,8-dihydro-8-hydroxy-7-phenyl-indeno[1',2':4,5]pyrido[2,1-a]isoindol-5-one (15a)

Mp 237–239°C; ^{1}HNMR ($CDCl_3$, 250 MHz) δ 7.98 (d, *J* = 7.3 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.66 (dt, *J* = 7.4, 1.9 Hz, 2H), 7.57 (dt, *J* = 7.4, 1.9 Hz, 2H), 7.50–7.38 (m, 2H), 7.18–7.05 (m, 3H), 6.82 (dd, *J* = 8.0, 1.9 Hz, 2H), 6.62 (d, *J* = 6.3 Hz, 1H), 6.32 (d, *J* = 6.3 Hz, 1H), 5.98 (brs, 1H, OH), 4.86 (d, *J* = 1.9 Hz, 1H); ^{13}CNMR ($CDCl_3$, 62.5 MHz) δ 170.7, 144.1, 142.0, 137.9, 137.4, 135.2, 135.1, 132.5, 129.9, 129.6, 128.9, 128.2, 127.7, 126.4, 124.9, 123.9, 121.0, 120.6, 113.6, 104.4, 81.4, 73.3 ppm. MS (70 eV): *m/z* (%) 363 (M$^+$, 95), 286 (100), 258 (32), 202 (20), 77 (55), 51 (30); HRMS *m/z*calcd for $C_{25}H_{17}NNaO_2$ (M + Na): 386.1151, found: 386.1176.

General procedure for the preparation of pentacycles (15)

An oven-dried resealable tube was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 5.0 mol %), XPhos ligand (24 mg, 0.05mmol, 5.0 mol %), 2-formylbenzeneboronic acid (750 mg, 5 mmol), K_3PO_4 (1.37 g, 7.0 mmol) and pyridine**10** or **14** (1.0 mmol). The flask was evacuated and backfilled with argon then degassed dioxane (6 mL) was added through the rubber septum. After heating for 12h at 100°C, the reaction mixture was cooled to room temperature, extracted with ethyl acetate (3 x 20 mL) and dried over $MgSO_4$. After filtration on Celite and concentration, the residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate) to give the pentacycles.

7,8-dihydro-8-hydroxy-7-(4-methoxy-phenyl)-indeno[1',2':4,5]pyrido[2,1-a]isoindol-5-one (15b)

Yield: 52% (102 mg); mp 159–161°C; ^{1}HNMR($CDCl_3$, 400 MHz) δ 7.94 (d, *J* = 7.2 Hz, 1H), 7.80–7.45 (m, 5H), 7.50–7.40 (m, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 6.2 Hz, 1H), 6.32 (d, *J* = 6.2 Hz, 1H), 5.94 (s, 1H), 4.91 (br s, 1H, OH), 3.65 ppm (s, 3H, OCH_3); ^{13}CNMR ($CDCl_3$, 100 MHz) δ170.6, 158.9, 144.0, 142.1, 137.2, 135.1, 134.9, 132.4, 129.95, 129.9, 129.5, 128.9, 127.65, 127.6, 124.8, 123.8, 121.0, 120.5, 113.6, 113.3, 104.4, 81.2, 72.7, 55.0 ppm. HRMS *m/z*calcd for $C_{26}H_{19}NNaO_3$ (M + Na): 416.1257, found: 416.1265.

7,8-dihydro-8-hydroxy-7-(4-methylthio-phenyl)-indeno[1',2':4,5]pyrido[2,1-a]isoindol-5-one (15c)

Yield: 50% (100 mg); mp 97–99°C; ^{1}HNMR ($CDCl_3$, 400 MHz) δ 7.94 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.68–7.62 (m, 2H), 7.60–7.54 (m, 2H), 7.48–7.38 (m, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 6.0 Hz, 1H), 6.33 (d, *J* = 6.0 Hz, 1H), 5.69 (m, 1H), 4.90 (d, *J* = 2.5 Hz, 1H, OH), 2.33 ppm (s, 3H, SCH_3); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 170.6, 143.9, 141.8, 138.0, 137.2, 135.1, 134.9, 134.7, 132.5, 129.9, 129.6, 128.9, 127.6, 126.9, 126.1, 124.8, 123.9, 121.0, 120.5, 113.5, 104.3, 81.3, 72.9, 15.4 ppm. HRMS *m/z*calcd for $C_{26}H_{19}NNaO_2S$ (M + Na): 409.1029, found: 432.1047.

7,8-dihydro-8-hydroxy-7-(4-formyl-phenyl)-7H-indeno[1',2':4,5]pyrido[2,1-a]isoindol-5-one (15d)

Yield: 71% (139 mg); mp 151–153°C; ^{1}HNMR ($CDCl_3$, 400 MHz) δ 9.85 (s, 1H, CHO), 7.95 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.70–7.63 (m, 2H), 7.62–7.54 (m, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.46 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 6.0 Hz, 1H), 6.32 (d, *J* = 6.0 Hz, 1H), 5.99 (d, *J* = 2.4 Hz, 1H), 4.84 ppm (d, *J* = 2.5 Hz, 1H, OH); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 191.6, 170.5, 144.8, 143.6, 141.0, 137.0, 135.5, 134.9, 132.7, 130.1, 129.7, 129.4, 129.2, 127.3, 127.1, 124.8, 123.9, 121.1, 120.6, 114.1, 104.3, 81.4, 73.1 ppm. HRMS *m/z*calcd for $C_{26}H_{17}NNaO_3$ (M + Na): 414.1101, found: 414.1107.

7,8-dihydro-8-hydroxy-7-(4-pyridyl)-7H-indeno[1',2':4,5]pyrido[2,1-a]isoindol-5-one (15f)

Yield (22%, 40 mg); mp 135–137°C; ^{1}HNMR($CDCl_3$, 200 MHz) δ 8.32 (d, *J* = 6.2 Hz, 2H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.78–7.51 (m, 5H), 7.50–7.40 (m, 2H), 6.70 (d, *J* = 6.2 Hz, 2H), 6.63 (d, *J* = 6.4 Hz, 1H), 6.33 (d, *J* = 6.4 Hz, 1H), 5.98 (s, 1H), 4.85 ppm (br s, 1H, OH); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 170.4, 149.1, 147.5, 143.4, 140.5, 136.8, 134.9, 134.85, 132.9, 130.3, 129.9, 129.3, 127.3, 124.9, 124.0, 121.5, 121.1, 120.7, 114.2, 104.1, 81.2, 72.7 ppm. HRMS *m/z*calcd for $C_{24}H_{17}N_2O_2$ (M + H): 365.1285, found: 365.1269.

Acknowledgements

This research is supported by CNRS, Université de Lorraine, Ministère de l'EnseignementSupérieur et de la Recherche (Grant to Z.C.), the European Commission ERC Starting Grant (PhotoSi, 278912) and MAE (DirezioneGenerale per la Promozione del Sistema Paese).The authors thank the Service Commun de Diffraction X (Université de Lorraine) for providing access to crystallographic experimental facilities.

Notes and references

[a]Laboratoire SRSMC, UMR CNRS 7565, Université de Lorraine, 54506 Vandoeuvre-les-Nancy, France.
[b]Department of Chemistry "G. Ciamician", University of Bologna. Via Selmi 2, 40126 Bologna, Italy. E-mail: paola.ceroni@unibo.it
[c]Laboratoire CRM2, UMR CNRS 7036, Université de Lorraine, 54506 Vandoeuvre-les-Nancy, France.
[d] New adress: Institut de Chimie de Strasbourg, UMR 7177, Equipe LASYROC, 1 rue Blaise Pascal, 67008 Strasbourg, France. E-mail: vmamane@unistra.fr

† Electronic Supplementary Information (ESI) available: [Copy of ^{1}H and ^{13}C NMR spectra of all compounds, ORTEP view of compounds**2**,**15a** and **15d**]. See DOI: 10.1039/b000000x/

‡ **2**: C21H17NO2, Mr=315.36, crystal dimensions: 0.19*0.15*0.09 mm, triclinic, space group *P*-1, a=8.3902(4)Å, b=9.4235(5)Å, c=10.5655(5)Å, α=68.634(5)°, β=86.055(4)°, γ=83.059(4)°V=771.97(7)Å^3, T=110(2) K, Z=2, ρ_{calcd}=1.357 g.cm^{-3}, μ=0.688 mm^{-1}, 8377 reflections collected, 3099 unique reflections, R_{int}=0.0408, $2\theta_{max}$=152.34°, 223 parameters, R_1=0.0636, wR_2=0.1703, ρmin = -0.241.e.Å^{-3}, ρmax = 0.359e.Å^{-3}.
15a: C25H17NO2, Mr=363.40, crystal dimensions: 0.23*0.18*0.09 mm, monoclinic, space group $P2_1/c$, a=10.6552(3)Å, b=8.1691(2)Å, c=20.6721(6)Å, β=104.472(3)°, V=1742.28(8)Å^3, T=110(2) K, Z=4, ρ_{calcd}=1.385 g.cm^{-3}, μ=0.702 mm^{-1}, 9695 reflections collected, 3235, unique reflections, R_{int}=0.0146, $2\theta_{max}$=140.26°, 254 parameters, R_1=0.0379, wR_2=0.0910, ρmin = -0.263.e.Å^{-3}, ρmax = 0.283e.Å^{-3}.
15d: 2(C26H17NO3), CH2Cl2, Mr=867.74, crystal dimensions: 0.20*0.14*0.09 mm, orthorhombic, space group $Pna2_1$, a=26.5772(4)Å, b=11.8718(2)Å, c=12.8742(2)Å, V=4062.06(11)Å^3, T=100(2) K, Z=4, ρ_{calcd}=1.419 g.cm^{-3}, μ=1.914 mm^{-1}, 40982 reflections collected, 7997, unique reflections, R_{int}=0.0151, $2\theta_{max}$=145.80°, 571 parameters, R_1=0.0356, wR_2=0.0961, refined inversion twin population parameter (Flack parameter) : 0.244(10). ρmin = -0.277.e.Å^{-3}, ρmax = 0.498e.Å^{-3}.

CCDC 1027766, CCDC 1027765 and CCDC 1027764contain the detailed crystallographic data of **2**, **15a** and **15d**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.ik/data_request/cif.

1 a) M. Shimizu and T. Hiyama, *Chem. Asian J.*, 2010, **5**, 1516. b) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.,* 2009, 4332 and references therein. c) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.,* 2011, **40**, 5361.
2 For some recent examples of highly luminescent solids, see: a) O. Bolton,K. Lee, H. J. Kim, K. Y. Lin and J. Kim, *Nature Chem.,* 2011, **3**, 205. b) G.Bergamini, A.Fermi, C.Botta, U.Giovanella, S.Di Motta, F.Negri, R.Peresutti, M.Gingras and P. Ceroni, *J. Mater. Chem. C*, 2013, **1**, 2717. c) L. Chen, Y. Jiang, H. Nie, P. Lu, H. H. Y. Sung, I. D. Williams, H. Sing Kwok, F. Huang, A. Qin, Z. Zhao and B. Z. Tang, *Adv. Funct. Mat.,* 2014, **24**, 3621.
3 a) Highly Efficient OLEDs with Phosphorescent Materials, ed: H. Yersin, 2007, Wiley-VCH Berlin. b) G. M. Farinola and R. Ragni, *Chem. Soc. Rev.*, 2011, **40**, 3467.
4 a) I. D. W. Samuel and G. A. Turnbull, *Chem. Rev.*, 2007, **107**, 1272. b) S. Forget and S. Chénais, Organic Solid-State Lasers, Springer Series in Optical Science, 2013, vol. 175. c) G. M. Akselrod, E. R. Young, K. W. Stone, A. Palatnik, V. Bulovic andY. R. Tischler, *Phys. Rev. B*, 2014, **90**, 035209.
5 See e.g.: a) S. W. Thomas, III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339. b) M. Schferling, *Angew. Chem. Int. Ed.*, 2012, **51**, 3532.
6 H. Langhals, T. Potrawa, H. Nöth and G. Linti, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 478.
7 Z. Chamas, O. Dietz, E. Aubert, Y. Fort and V. Mamane, *Org. Biomol. Chem.*, 2010, **8**, 4815.
8 Z. Chamas, E. Marchi, A. Modelli, Y. Fort, P. Ceroni and V. Mamane, *Eur. J. Org. Chem.*, 2013, 2316.
9 P. Eastwood, J. Gonzalez, S. Paredes, A. Nueda, T. Domenech, J. Alberti andB. Vidal, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 1697.
10 V. Mamane and Y. Fort, *Tetrahedron Lett.*, 2006, **47**, 2337.
11 V. Mamane, F. Louërat, J. Iehl, M. Abboud andY. Fort, *Tetrahedron*, 2008, **64**, 10699.
12 The stability of **16** was however reduced in solution which prevented obtaining clean ^{13}C NMR analysis.
13 For a review, see: R. Martin andS. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461.
14 For an example from our laboratory, see: M. Abboud, E. Aubert and V. Mamane, *Beilstein J. Org. Chem.*, 2012, **8**, 253.
15 J. N. Demas and G. A. Crosby,*J. Phys. Chem.*, 1971, **75**, 991.
16 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi in Handbook of Photochemistry, ed. Taylor & Francis, London, 3rd edn., 2006, ch. 10.
17 J. C. De Mello,H. F. Wittmannand R.H. Friend,*Adv. Mater.*, 1997, **9**, 230.
18 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
19 G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.