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Synthesis, structures, optical properties, and TD-DFT studies of donor-π-conjugated dipicolinic acid/ester/amide ligands

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Abstract

A series of 2,6- and 4-functionalized dipicolinic acid, ester, or amide featuring π-conjugated substituents such as donor-(phenyl or fluorenyl)-acetylene groups have been synthesized. Four crystallographic structures are reported. The influence of the substituent position, the nature of the donor group, and the conjugated backbone as well as the role of the pyridinic side arms on the absorption and emission properties are studied and discussed on the basis of TD-DFT calculations.

1. Introduction

Dipicolinic acid is a widely used building block in coordination and supramolecular chemistry. The corresponding bis-acid (DPA), bis-ester (DPE), and bis-amide (DPAM) derivatives behave as tridentate ligands, which efficiently coordinate to transition metals (Zn^{II}, Cu^{II}, Pt^{II}, Mn^{II}, Ru^{II}, $Co^{II/III}$, Fe^{III},…) or lanthanides.[1–3] Recently, the use of such ligands was extended to the formation of complexes featuring interesting luminescence,[4] nonlinear optical[5] or magnetic properties,[6] in solution as well as in crystalline state[7] or sol–gel matrix.[8] In addition, unsymmetrical acid/amide ligands were recently designed for heavy metal extraction purpose.[9] DPA has also been largely used as starting building block for the construction of supramolecular architectures like dendrimers,[10] cryptans,[11] calixarenes,[12] helicoidal polynuclear complexes,[13] even chiral[14] or self-assembled organic simple or double helix.[15]

Whereas DPA has already been substituted by functional or solubilizing group,[16] it has scarcely been involved for the design of chromophore-based ligands upon adequate functionalization by π-conjugated groups. To date, only phenyl,[17] phenylacetylene,[11,18] and oligo-thiophene[19] derivatives were reported and their photophysical properties studied. Recently, we thought to use DPAM as acceptor moiety for the design of new push–pull chromophores. Preliminary results underlined their interesting luminescence and nonlinear optical properties (second harmonic generation and two-photon absorption induced luminescence), and made them attracting candidates for biological imaging applications[20] as well as for the sensitization of Eu^{III} luminescence by two-photon antenna effect.[21]

In this article, we report the detailed synthetic procedures for the preparation of DPA/DPE/DPAM-based dipolar chromophores. The charge transfer can be induced either by direct functionalization of the 4-position of the pyridinic ring or by 2,6-substitution of the amido moieties of DPAM (Chart 1). A particular attention has been devoted to the optimization and multi-gram scale-up of the synthesis of key intermediates such as the iodo DPAM or DPE derivatives. Four crystallographic structures are described and the absorption/emission properties are studied and discussed on the basis of TD-DFT calculations.

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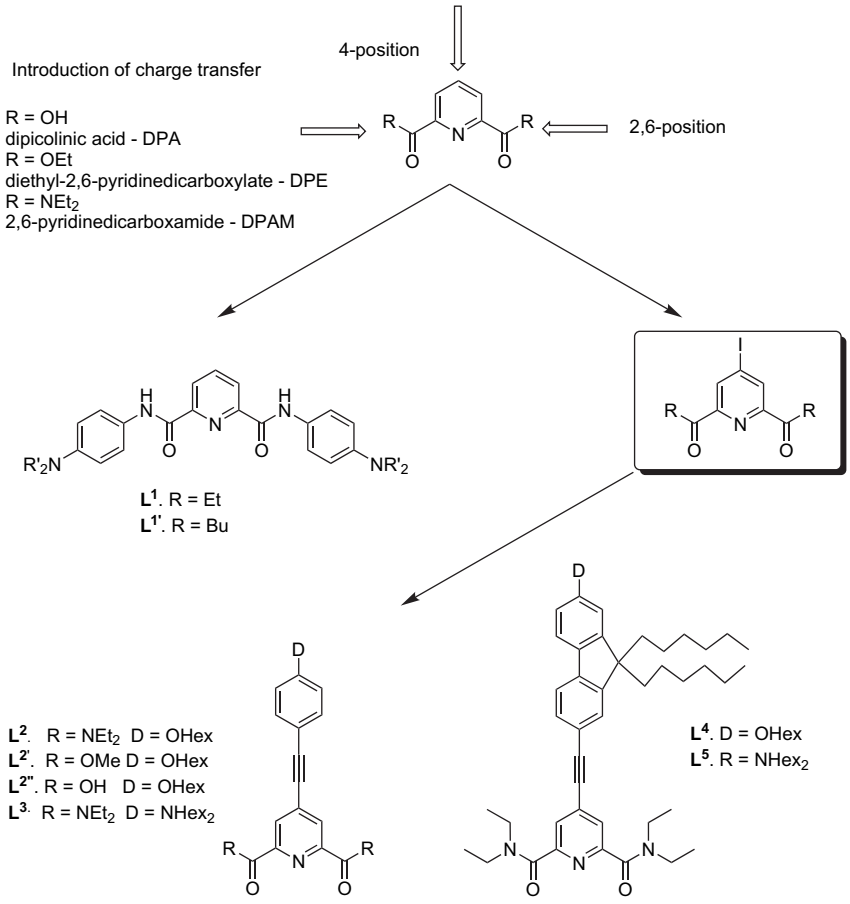
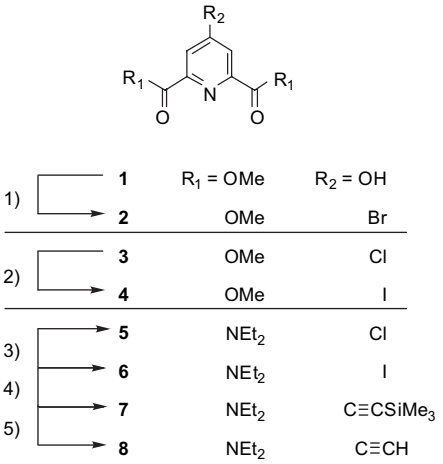


Chart 1. DPA/DPE/DPAM-based chromophores.

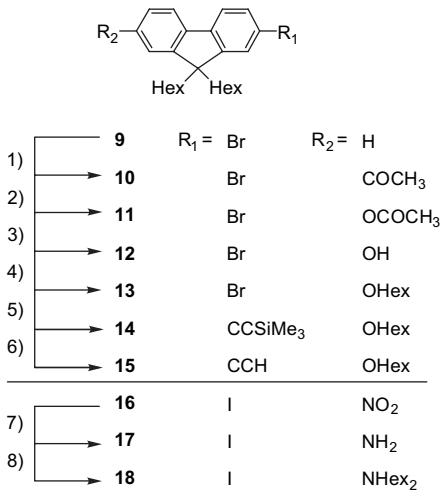
2. Results and discussion

2.1. Syntheses

Commercially available chelidamic acid is the starting building block for the synthesis of this series of tridentate ligands. As the presence of the pyridinic electron-withdrawing group *para* to the OH group significantly enhances the rate of nucleophilic substitutions, various halogens can be introduced at this position. Since the π-system functionalization in 4-position involves Pd-catalyzed Sonogashira cross-coupling reaction, we envisaged to prepare the bromo (**2**) or the more reactive iodo (**4**,**6**) derivatives (Scheme 1). Bromination reactions on chelidamic acid are generally carried out under harsh conditions, using PBr_3, PBr_5, or $POBr_3$.[22] We thus decided to revisit and adapt an original and milder bromination method for the synthesis of DPA and DPE derivatives.[23] This technique consists in the reaction of an excess of tetrabutylammonium bromide with **1** in hot toluene for 4 h in the presence of P_4O_{10}. After workup, pure **2** was isolated as a white-beige powder in 85% yield. Unfortunately, further reactivity of **2** for the synthesis of $\mathbf{L^{2'}}$ by Sonogashira coupling was below our expectations, reaching only 45% of the desired ligand. The synthesis of the iodo derivative **4** from **3** was adapted and optimized from the literature to avoid decomposition of the final product **4** (sonication duration was reduced to 30 min).[24] DPAM derivative **6** was obtained from **5** in fairly good yield (72%) in the presence of phosphorous acid and a 57% aqueous solution of hydrogen iodide. In order to avoid the hydrolysis of the amido moieties by hydrogen iodide, new reaction conditions were found to optimize the yield of this reaction (see Section 4).[25] Note that **4** and **6**, which are the two



Scheme 1. Synthesis of DPA, DPE, and DPAM intermediates: (1) NBu_4Br, P_4O_{10}, toluene, sonication, 110 °C, 30 min, 81%; (2) CH_3COCl, NaI, CH_3CN, sonication, rt, 30 min, 95%; (3) HI, H_3PO_3, H_2O, 80 °C, 210 min, 72%; (4) $PdCl_2(PPh_3)_2$, CuI, Et_3N/THF, rt, 20 h, 92%; (5) K_2CO_3, CH_2Cl_2, MeOH, rt, 90 min, 94%.



Scheme 2. Synthesis of fluorene π-donor intermediate building blocks: (1) CH_3COCl, $AlCl_3$, CH_2Cl_2, rt, 20 h, 93%; (2) *m*-CPBA, $CHCl_3$, rt, 4 days, 82%; (3) KOH, H_2O, MeOH, 80 °C, 20 h, 97%; (4) *n*-Hex–Br, K_2CO_3, CH_3CN, 82 °C, 20 h, 85%; (5) $PdCl_2(PPh_3)_2$, CuI, Et_3N/DMF, 115 °C, 3 days, 84%; (6) K_2CO_3, CH_2Cl_2, MeOH, rt, 90 min, 95%; (7) Fe powder, AcOH, 118 °C, 30 min, 69%; (8) *n*-Hex–Br, NaI, Na_2CO_3, DMF, 95 °C, 20 h, 71%.

key synthons, could be prepared in a several gram scale (for example, 10 g for **4**) by using our modified procedures. At this stage, the classical Sonogashira reaction between **6** and trimethylsilylacetylene (TMS-acetylene) followed by TMS deprotection with K_2CO_3 led to the formation of compounds **7** and **8** in 92% and 94% yields, respectively (Scheme 1).

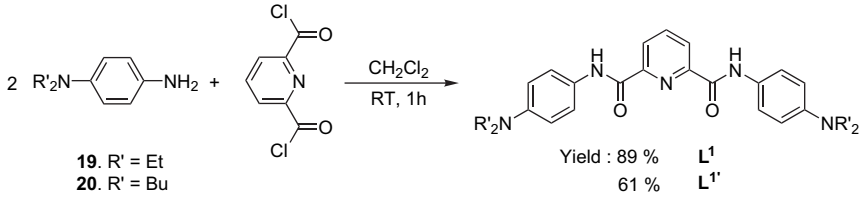
The hexyloxyfluorenylacetylene intermediate **15** was obtained in six steps with a good overall yield (50%) by following the procedure proposed by Serrano et al. (Scheme 2).[26] Commercially available 2-bromofluorene was first C-alkylated to compound **9**, which gave **10** after a Friedel–Crafts acylation. This compound was easily rearranged to **11** by a Baeyer–Villiger oxidation using *m*-CPBA and a further deprotection of the newly formed ester function with KOH led to **12**. O-Alkylation of the alcohol function with bromohexane produced **13**, which then led to **14** after a Sonogashira reaction with TMS-acetylene and finally to **15** after deprotection of the TMS group. In contrast, the synthesis of the nitrogen donating fluorene intermediate **18** was more straightforward: in the first step, commercially available 2-iodo-7-nitrofluorene was C-alkylated by bromohexane under basic conditions to lead to **16**, then the reduction reaction of the nitro group to the amino derivative **17** using Fe powder and a final N-alkylation with bromohexane produced **18**.[27,28]

The most straightforward approach in order to induce strong charge transfer onto the pyridinic moieties of the ligands remains the direct amidation of the acidic side arms. In the first step, the acyl chloride derivative of dipicolinic acid was obtained in situ by the action of thionyl chloride in the presence of catalytic amount of DMF. After removal of the solvents, 2-fold excess of either the commercially available amine **19** or **20**[29] was added yielding 89% and 61% of $\mathbf{L^1}$ and $\mathbf{L^{1'}}$, respectively (Scheme 3). The second approach for the synthesis of the ligands consisted in the functionalization at the 4-position of the pyridine by a Sonogashira cross-coupling reaction using standard experimental conditions ($PdCl_2(PPh_3)_2$: 10 mol %; CuI: 20 mol %; THF/NEt_3; temperature: 40 °C). Six new ligands were synthesized using this technique ($\mathbf{L^2}$, $\mathbf{L^{2'}}$, $\mathbf{L^{2''}}$–$\mathbf{L^5}$) and isolated after column chromatography with moderate to good yields (50–90%, Scheme 4). Detailed experimental procedures and spectroscopic and analytic characterizations are described in Section 4.

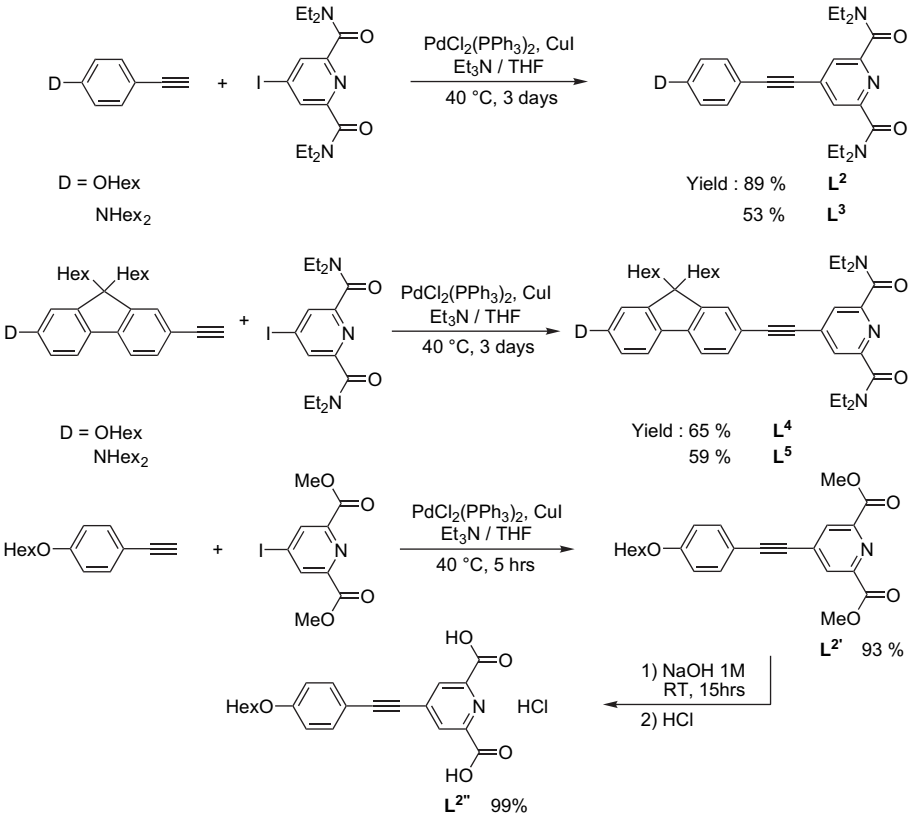
2.2. Crystallographic structures

Crystals suitable for X-ray diffraction analysis were obtained in the cases of $\mathbf{L^1}$, $\mathbf{L^2}$, $\mathbf{L^{2'}}$, and $\mathbf{L^3}$ by slow evaporation of dichloromethane solutions. Crystal data and refinement parameters are collected in Table 1; ORTEP drawing and selected bond lengths and angles are described in Figure 1 and Table 2, respectively. In the case of $\mathbf{L^1}$, the crystallographic packing is ensured by a network of intermolecular hydrogen bonds between the NH of the amide fragment and the carbonyl of a vicinal molecule with short contact interactions of about 2.156 and 2.174 Å. In addition, the molecular structure indicates the exclusive formation of the *syn–syn* conformer due to the presence of two intramolecular hydrogen bonds between the amide fragment and the nitrogen atom belonging to the central pyridinic ring with $d(NH\cdots N_{py})$ of about 2.36 and 2.28 Å, respectively. The formation of these five member rings is responsible for the good planarity between the carboxamide side arms and the central pyridinic ring with twist angles τ of 6.22 and 7.76°. Similar structures have already been described in the literature in the case of phenyl[30] or benzyl[31] substituted amides.

On the other hand, the absence of any hydrogen bond source in the case of $\mathbf{L^2}$, $\mathbf{L^{2'}}$, and $\mathbf{L^3}$ results in a completely different crystal packing. The three dipolar ligands crystallize in a head-to-tail way in order to minimize the electrostatic repulsion and the crystal cohesion is mainly ensured by π-stacking interactions. The difference observed between the three structures mainly consists in distortion due the sterical crowding of the alkyl substituents. In consequence, ligand $\mathbf{L^{2'}}$ featuring the less bulky methyl ester substituent exhibits the most planar structure with small twist angles between ester and pyridinic groups (τ=2.80 and 4.24°), as well as between



Scheme 3. Synthesis of 2,6- functionalized DPAM derivatives.



Scheme 4. Synthesis of the 4-functionalized ligands.

Table 1
Selected crystallographic data and collection parameters for $\mathbf{L^1}$, $\mathbf{L^2}$, $\mathbf{L^{2'}}$, and $\mathbf{L^3}$

Compound	$\mathbf{L^1}$	$\mathbf{L^2}$	$\mathbf{L^{2'}}$	$\mathbf{L^3}$
Formula	$C_{35}H_{52}N_4O_2$	$C_{29}H_{39}N_3O_3$	$C_{23}H_{25}NO_5$	$C_{27}H_{33}N_5O_2$
M/g	560.81	477.63	395.44	459.58
Crystal size/mm	0.28×0.24×0.16	0.45×0.45×0.40	0.45×0.33×0.33	0.32×0.22×0.22
Color	Yellow	White	White	Green
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	Pbcn	$P2_1/c$	$P-1$	$P2_1/a$
a/Å	15.5771 (6)	8.8634 (4)	5.4095 (1)	9.7048 (2)
b/Å	18.5939 (9)	27.728 (1)	7.6784 (1)	14.5440 (3)
c/Å	11.5586 (5)	11.3235 (5)	25.9772 (5)	17.7686 (3)
α/°	90	90	93.643 (1)	90
β/°	90	100.174 (3)	94.868 (1)	97.7690 (10)
Γ/°	90	90	105.335 (1)	90
V/Å^3	3347.8 (3)	2739.0 (2)	1032.67 (3)	2484.96 (8)
Z	4	4	2	4
λ (Mo Kα)/Å	0.71073	0.71073	0.71073	0.71073
μ/cm^{-1}	0.69	0.75	0.90	0.80
F(000)	1224	1032	420	984
T/K	120	120	120	130
D_c/g cm^{-3}	1.113	1.158	1.272	1.228
θ range/°	3.10–26	3.21–27.0	2.80–27.46	2.54–29.18
hkl ranges	$0<h<19$, $0<k<22$, $0<l<14$	$-10<h<11$, $-35<k<35$, $-13<l<14$	$0<h<7$, $-9<k<9$, $-33<l<32$	$0<h<13$, $0<k<19$, $-24<l<23$
Variables	190	317	262	314
Reflections measured	3285	5931	4574	6639
Reflections [$I>2\sigma(I)$]	2484	5092	3765	4956
$R1[I>2\sigma(I)]$/$R1$ (all data)	0.0502/0.0709	0.0472/0.0563	0.0590/0.0710	0.0567/0.0806
$wR2[I>2\sigma(I)]$/$wR2$ (all data)	0.1320/0.1564	0.1143/0.1207	0.1690/0.1838	0.1496/0.1722
Sw	0.997	1.045	1.016	1.060
Largest diff peak/hole/e Å^{-3}	0.287/−0.213	0.347/−0.181	0.470/−0.329	0.435/−0.263

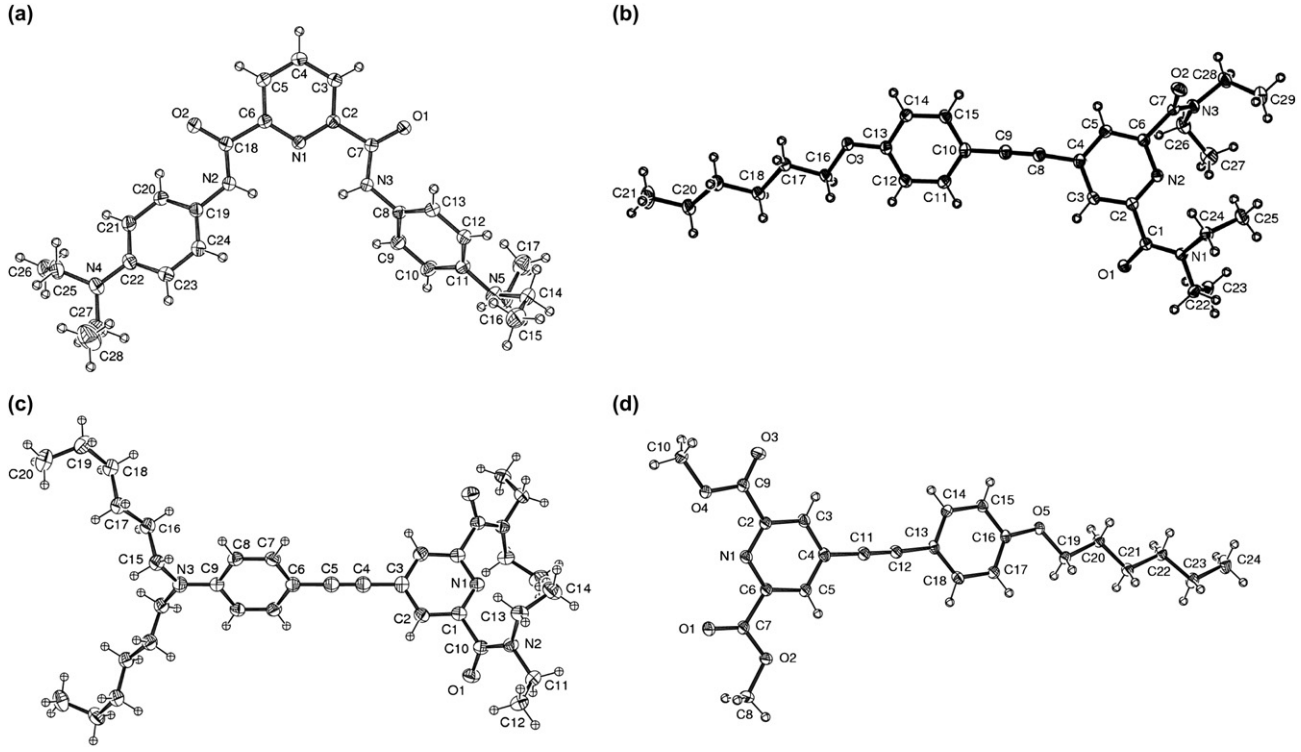


Figure 1. ORTEP drawings of ligands $\mathbf{L^1}$ (a), $\mathbf{L^2}$ (b), $\mathbf{L^{2'}}$ (d), and $\mathbf{L^3}$ (c).

alkoxyphenyl and pyridinic moieties (ρ=5.88°, Table 2). Replacing the ester by diethylamide fragment ($\mathbf{L^2}$) induces a significant steric hindrance at the acceptor side of the molecule. This modification results in a small distortion of the π-conjugated backbone (ρ=15.81°), and a strong deformation of the pyridine-dicarboxamide unit with twist angles τ of 30.64 and 65.29°. Finally, changing the hexyloxy by a dihexylamino donor group ($\mathbf{L^3}$) strongly enhances the steric hindrance at both donor and acceptor sides of the molecule. These sterical crowding dramatically distorts the π-conjugated backbone as well as the pyridine-dicarboxamide moieties with twist angles τ and ρ of 55.7 and 48.5°, respectively. It is worth noting that all these deformations are clearly due to the crystal packing, the molecule being completely planar in solution as suggested by theoretical simulations (vide infra).

Table 2
Selected distances (Å) and angles (°)

	$\mathbf{L^1}$	$\mathbf{L^2}$	$\mathbf{L^{2'}}$	$\mathbf{L^3}$
Conformation	*syn–syn*	*syn–syn*	*syn–anti*	*syn–syn*
τ[a]	6.22	30.64	2.80	48.52[d]
	7.76	65.29	4.24	
Φ[b]	34.43	—	—	—
	47.56			
ρ[c]	—	15.81	5.88	55.70
Cpy–C(O)	1.5069(17)	1.5123(19)	1.510(2)	1.513(2)[d]
	1.5064(18)	1.5147(18)	1.5149(19)	
C=O	1.2375(15)	1.2285(18)	1.1987(17)	1.234(2)[d]
	1.2267(16)	1.2437(16)	1.2051(18)	
C(O)–N	1.3507(18)	1.3486(19)	—	1.345(2)[d]
	1.3394(16)	1.3511(17)		
C≡C	—	1.202(2)	1.192(2)	1.186(4)
Cpy–(CC)	—	1.4352(18)	1.4385(19)	1.443(3)
(CC)–Cph	—	1.4363(19)	1.4379(18)	1.437(3)

[a] Twist angle between the central pyridinic ring and the lateral amide or ester arm.
[b] Twist angle between the diethylaminophenyl and the carboxamide.
[c] Twist angle between the pyridinic and the 4-functionalized phenyl ring.
[d] The two lateral arms of the molecule are symmetric due to the presence of a C_2 symmetric axis in the crystallographic structure.

2.3. Optical properties and TD-DFT calculations

Room temperature absorption and emission spectra of $\mathbf{L^1}$–$\mathbf{L^5}$ in diluted dichloromethane solution are displayed in Figures 2, 4, and 6 and the experimental and theoretical data are reported in Table 3. All chromophores exhibit broad

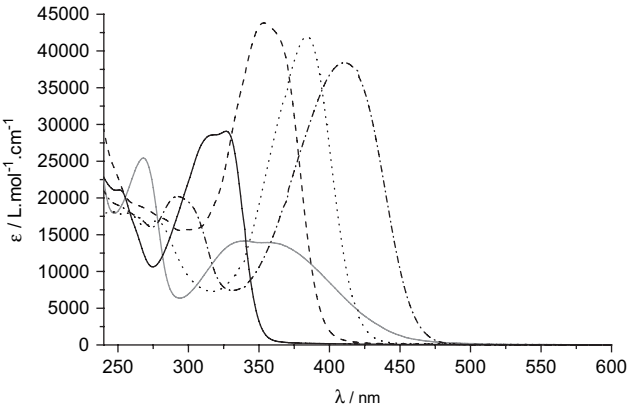


Figure 2. Absorption spectra of $\mathbf{L^1}$ (gray), $\mathbf{L^2}$ (—), $\mathbf{L^3}$ (···), $\mathbf{L^4}$ (---), and $\mathbf{L^5}$ (-·-) in dichloromethane.

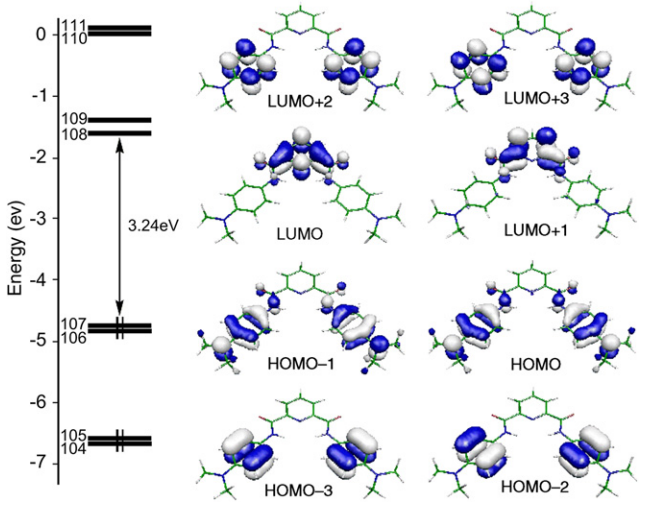


Figure 3. MO energy diagram of $\mathbf{L^{1a}}$.

intense structureless absorption transitions in the visible part of the spectra, with λ_{max} between 327 and 411 nm depending on the nature of the donor and transmitter groups. Two different behaviors can be distinguished depending on the 2,6- or 4-functionalization of the central pyridinic moieties. For the 2,6-functionalized ligands $\mathbf{L^1}$,$\mathbf{L^{1'}}$ a very broad transition centered at 341 nm with a shoulder at around 330 nm can be observed. DFT calculations (Fig. 3) performed on a model $\mathbf{L^{1a}}$ featuring dimethylamino donor group show two almost degenerated HOMOs (orbitals 106 and 107 in Fig. 3) and two quasi-degenerated LUMOs (orbitals 108 and 109). Therefore, two slightly different transitions are predicted theoretically at 420 and 405 nm, respectively (Table 3), and present a marked charge transfer (CT) character from the amino donor group to the central acceptor moieties delocalized on the pyridinic ring and on the carbonyl fragment. It is worth noting that the experimental transitions are significantly blue shifted compared to the calculated ones ($\Delta\lambda \approx 80$ nm). The overestimation of the calculated results is clearly due to the completely planar conformation of the dimethylaminophenylamide side arm obtained by geometry optimization ensuring an optimal

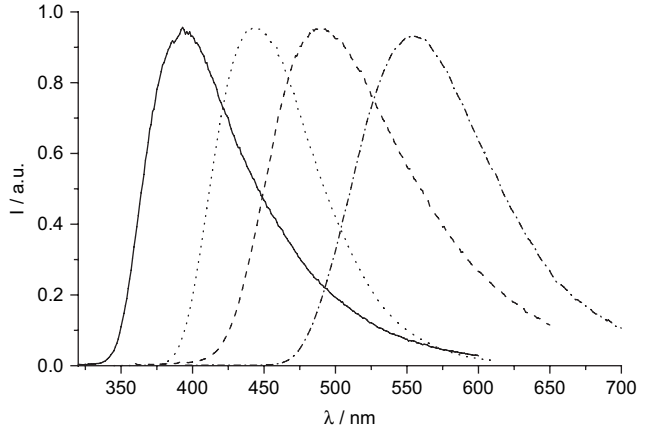


Figure 4. Luminescence spectra of $\mathbf{L^2}$ (—), $\mathbf{L^3}$ (···), $\mathbf{L^4}$ (---), and $\mathbf{L^5}$ (-·-) in dichloromethane with λ_{ex}=310, 340, 320, and 360 nm, respectively.

Table 3
Photophysical data in dichloromethane solution and from TD-DFT calculations

	λ_{abs}/ nm	ε/ L Mol^{-1} cm^{-1}	λ_{em}/ nm	λ_{max}^{calcd}/ nm	f[a]	Composition
$\mathbf{L^1}$	341	14,100	n			
$\mathbf{L^{1'}}$	341	14,100	n	420	0.16	HOMO→LUMO+1(0.66)
				405	0.26	HOMO-1→LUMO+1(0.66)
						HOMO→LUMO (0.15)
$\mathbf{L^2}$	327	29,100	394	333	0.99	HOMO→LUMO (0.65)
$\mathbf{L^{2'}}$	336	20,400	428	339	0.83	HOMO→LUMO (0.66)
$\mathbf{L^{2''}}$	346	25,700	461	344	0.76	HOMO→LUMO (0.66)
$\mathbf{L^3}$	384	42,000	443	370	1.00	HOMO→LUMO (0.66)
$\mathbf{L^4}$	354	43,800	489	378	1.24	HOMO→LUMO (0.66)
$\mathbf{L^5}$	411	38,400	554	422	1.03	HOMO→LUMO (0.67)

n: no emission.
[a] Calculated oscillator strength.

delocalization. On the contrary, in solution (or in the solid state), the free rotation around the (O)CNH–($PhNMe_2$) bond breaks this planarity and reduces the conjugation between the donor and the acceptor moieties.

On the other hand, all the 4-functionalized derivatives $\mathbf{L^2}$–$\mathbf{L^5}$ are good fluorophores with broad absorption *and* emission bands centered in the visible part of the spectra. In all cases, TD-DFT calculations performed on models featuring simplified alkyl substituents indicate that the lowest energy transition can be unambiguously assigned to a CT transition as illustrated by a representative example in the case of $\mathbf{L^{4a}}$ (Table 3 and Fig. 5). The calculated maximal absorption wavelengths, λ_{max}^{calcd}, match perfectly the experimental ones (Table 3). As expected, increasing the donor strength or the π-conjugated length by replacing the alkoxy ($\mathbf{L^2}$,$\mathbf{L^4}$) by an amino group ($\mathbf{L^3}$,$\mathbf{L^5}$) or a phenyl ($\mathbf{L^2}$,$\mathbf{L^3}$) by a fluorenyl ($\mathbf{L^4}$,$\mathbf{L^5}$) moiety, respectively, results in a bathochromic shift of both absorption and emission bands. In consequence, these simple chemical modifications allow to tune the emission properties on a large range from the blue (350 nm) to the red (650 nm) as shown in Figure 4.

Finally, it is possible to fine tune the photophysical properties by subtle modifications of the pyridinic side arms. Replacing bis-diethylamide moieties of ligand $\mathbf{L^2}$ by di-(methyl

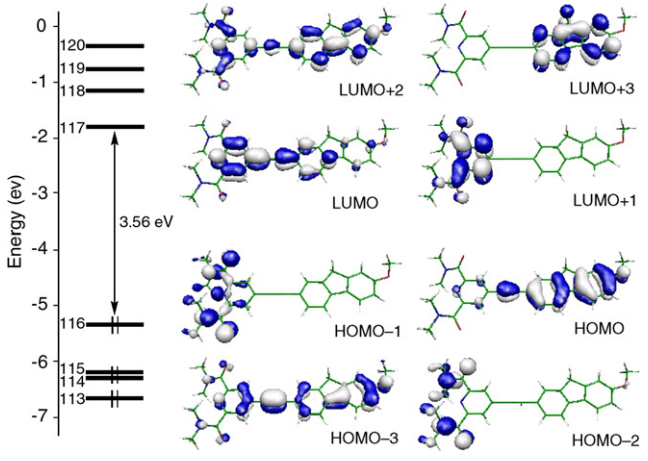


Figure 5. MO energy diagram of $\mathbf{L^{4a}}$.

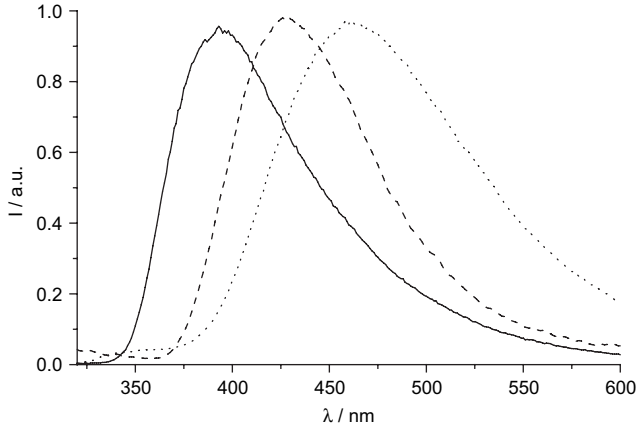


Figure 6. Luminescence spectra of $\mathbf{L^2}$ (—), $\mathbf{L^{2'}}$ (---), and $\mathbf{L^{2''}}$ (···) in dichloromethane with λ_{ex}=310 nm.

ester) $\mathbf{L^{2'}}$ or di-acid $\mathbf{L^{2''}}$ results in a 10 nm red shift in absorption for each modification (Table 3). This bathochromic shift is much more significant in emission (Fig. 6): a large red shift ($\Delta\lambda_{em}$=65 nm) is observed from $\mathbf{L^2}$ to the di-acidic derivative $\mathbf{L^{2''}}$. This effect can be rationalized on the basis of the theoretical calculations. Whereas, the three compounds present similar HOMOs, essentially located on the donor alkoxyphenyl part of the molecule, their LUMOs depicted in Figure 7 exhibit slight differences. In the case of $\mathbf{L^{2a}}$, the LUMO is delocalized on the pyridinic ring and on the triple bond without any significant participation of the amide fragment. On the contrary, the LUMOs of $\mathbf{L^{2'a}}$ and $\mathbf{L^{2''a}}$ show a strong participation of the carbonyl moieties, enforcing the acceptor character of the pyridinic ring. These last considerations could allow to conclude by the following order for the strength of the acceptor groups DPA>DPE>DPAM.

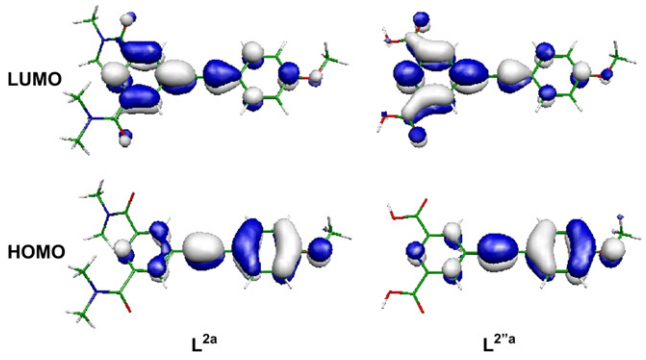


Figure 7. Comparison of HOMO and LUMO of $\mathbf{L^{2a}}$ and $\mathbf{L^{2''a}}$.

3. Conclusion

In summary, a series of 2,6- and 4-functionalized chromophore-based dipicolinic acid, ester, or amide molecules were prepared and four of them were characterized by X-ray diffraction. The photophysical studies and TD-DFT calculations clearly indicate that all compounds exhibit intense charge transfer from the donor end group to the central pyridinic acceptor fragment. Absorption and emission properties are tuned in all the visible range by modification of (i) the position of the substituents (2,6- or 4-), (ii) the nature of the donor end group (amino or alkoxy), (iii) the nature of the π-conjugated backbone (phenyl, phenylacetylene, fluorenylacetylene), and (iv) the nature of the pyridinic side arms (acid, ester, amide). Preliminary experiments have underlined the interesting nonlinear optical properties (two-photon absorption and second harmonic generation) of some of these compounds and further studies are currently in progress to adapt these chromophores for biological imaging purpose.[20] Finally, all these chromophores are also ligands that are able to coordinate a large variety of transition metals or lanthanides. The systematic study of the nonlinear optical properties of the related complexes is under investigation.

4. Experimental section

4.1. General procedure

NMR spectra (^{1}H, ^{13}C) were recorded at room temperature on a BRUKER AC 200 operating at 200.13 and 50.32 MHz for ^{1}H and ^{13}C, respectively. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (^{1}H, ^{13}C); residual solvent peaks of the deuterated solvents were used as internal standard. UV–vis absorption measurements were recorded on a JASCO V550 spectrometer. The luminescence spectra were measured using a Horiba–Jobin Yvon Fluorolog-3® spectrofluorimeter, equipped with a red-sensitive Hamamatsu R928 photomuliplier tube. Spectra were reference corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating). Infra-red spectra were recorded on a Mattson 3000 spectrometer using KBR pellets. High-resolution mass spectrometric measurements and elemental analysis were performed at the Service Central d'Analyse du CNRS (Vernaison, France).

Crystal structure analyses were performed on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized Mo Kα radiation. Cell parameters were obtained with Denzo and Scalepack with 10 frames (psi rotation: 1°/frame). The structure was solved with SIR-97,[32] which reveals the nonhydrogen atoms of structure. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined with SHELXL97[33] by the full-matrix least-square techniques (use of F magnitude; x, y, z, α_{ij} for C, N, and O atoms, x, y, z in riding mode for H atoms). ORTEP views were made with PLATON 98.[34] All calculations were performed on a Silicon Graphics Indy computer. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 233716, CCDC 282663, CCDC 278081, and CCDC 238186.

Computational details. DFT geometric optimizations and TD-DFT excitation energy calculations on simplified ligands featuring a methyl substituent were carried out with the Gaussian 03 (Revision B.04) package[35] employing the three-

parameter hybrid functional of Becke based on the correlation functional of Lee, Yang, and Parr (B3LYP).[36] The 6−31G* basis sets were used for all atoms.

4.2. Synthesis

4-Hydroxy-2,6-pyridinedicarboxylic acid dimethyl ester **1**,[37] 4-chloro-2,6-pyridinedicarboxylic acid dimethyl ester **3**,[38] 2-bromo-9,9-dihexylfluorene **9**,[39] 4-ethynyl-*N*,*N*-dihexylaniline,[40] 2-iodo-7-nitro-fluorene **16**,[41] and *N*,*N*-dibutyl-1,4-benzenediamine **20**[29] were prepared by following the published procedure. Chelidamic acid, *N*,*N*-diethyl-1,4-benzenediamine, and 4-(hexyloxy)phenylacetylene were commercially available, and purchased from Aldrich, Acros, and Maybridge, respectively. All the solvents used for the synthesis were of analytical grade. For the spectroscopy, spectroscopic grade solvents were used.

4.2.1. General procedure A for Sonogashira cross-coupling

To a degassed solution of the halogenated substrate in THF (DMF) and Et_3N under argon are added the acetylene derivative, copper iodide, and $Pd(PPh_3)_2Cl_2$. The dark brown mixture is heated in the dark while stirring. After cooling to room temperature, the black precipitate is filtered and triturated with CH_2Cl_2 (2×20 mL). The remaining organic phase is washed with saturated aqueous ammonium chloride solution (3×50 mL) and brine (50 mL). The organic layer is dried (Na_2SO_4) and evaporated under vacuum. The crude residue is purified by flash chromatography on silica.

4.2.2. 4-Bromo-2,6-pyridinedicarboxylic acid dimethyl ester (*2*)

Tetrabutylammonium bromide of 38.2 g (118.9 mmol, 5.0 equiv), 42.4 g of P_4O_{10} (147.2 mmol, 6.0 equiv), and 150 mL of dry toluene are introduced in a 500 mL flask. The mixture is heated to 80 °C for an hour. 4-Hydroxy-2,6-pyridinedicarboxylic acid dimethyl ester of 5 g (23.7 mmol, 1 equiv) is dissolved in 150 mL of dry toluene and slowly added to the reaction. The resulting mixture is heated to 110 °C for 4 h. After cooling to room temperature, the supernatant is taken aside while remaining oily residue is triturated with 200 mL of hot toluene for an hour. The organic phases are combined, poured into 250 mL of water, and the mixture is stirred for additional 2 h. The organic phase is then dried over Na_2SO_4 and evaporated. The product is obtained as a white-beige powder (5.5 g, 85%). Mp 176 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 8.47 (2H, s, Ph), 4.04 (6H, s, 2×COOCH_3).

4.2.3. 4-Iodo-2,6-pyridinedicarboxylic acid dimethyl ester (*4*)

Sodium iodide of 65.2 g (435 mmol, 10 equiv) is added to a solution of 4-chloro-2,6-pyridinedicarboxylic acid dimethyl ester (10 g, 43.5 mmol, 1 equiv) in acetonitrile (300 mL). The mixture is sonicated for 20 min at room temperature. Acetyl chloride of 10.25 g (130.5 mmol, 3 equiv) is slowly added to the solution and the mixture is sonicated for an additional 30 min at room temperature. CH_2Cl_2 (300 mL) and saturated aqueous Na_2CO_3 (150 mL) are added. The organic phase is washed with saturated aqueous $Na_2S_2O_3$ (150 mL), water (150 mL), brine (150 mL), and dried over Na_2SO_4. After evaporation of the solvents and recrystallization from methanol, the product is obtained as a white powder (13 g, 93%). Mp 175 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 8.67 (2H, s, Ph), 4.03 (6H, s, 2×COOCH_3).

4.2.4. 4-Chloro-2,6-bis(diethylcarbamoyl)pyridine (*5*)

DMF (0.5 mL, 6.5 mmol) is added to a solution of chelidamic acid monohydrate (5.63 g, 28.0 mmol) in thionyl chloride (20 mL, 280 mmol). After stirring the mixture overnight at 76 °C, the excess of thionyl chloride is evaporated by trap-to-trap vacuum distillation technique. The remaining white residue is dissolved in dichloromethane (15 mL) and dry diethylamine (29 mL) is slowly added at 0 °C. The solution is heated to 55 °C for 2 h. Water (20 mL) is then added and the mixture is acidified to pH=1. After separation, the aqueous phase is extracted twice with dichloromethane (2×20 mL). The organic phases are combined, washed with water, saturated aqueous $NaHCO_3$, and dried over Na_2SO_4. After filtration and evaporation of the solvent, a white solid is obtained (8.07 g, 93%). (Found: C, 57.7; H, 7.2; N, 13.4. $C_{15}H_{22}ClN_3O_2$ requires: C, 57.8; H, 7.1; N, 13.5%.) Mp 116 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.61 (2H, s, Ph), 3.52 (4H, q, *J* 7.1, 2×NCH_2CH$_3$), 3.30 (4H, q, *J* 7.1, 2×NCH_2CH$_3$), 1.22 (6H, t, *J* 7.1, 2×NCH$_2$CH_3), 1.13 (6H, t, *J* 7.1, 2×NCH$_2$CH_3). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 166.8, 154.8, 146.1, 124.1, 43.2, 40.3, 14.2, 12.7.

4.2.5. 4-Iodo-2,6-bis(diethylcarbamoyl)pyridine (*6*)

To a mixture of 4-chloro-2,6-bis(diethylcarbamoyl)pyridine (3.0 g, 9.6 mmol, 2 equiv) and phosphorous acid (395 mg, 4.8 mmol, 1 equiv) is added drop by drop a 57% aqueous solution of hydrogen iodide (11.7 mL, 85.6 mmol, 18 equiv) at 0 °C. The reaction mixture is heated to 80 °C for 3.5 h. After cooling to room temperature, the mixture is neutralized by the slow addition of a saturated aqueous solution of $NaHCO_3$. The aqueous phase is extracted with diethyl ether (3×50 mL), and the organic phases are combined and dried over Na_2SO_4. The solvent is evaporated and the pure product is obtained as a light yellow solid (2.8 g, 72%). (Found: C, 44.9; H, 5.6; N, 10.3. $C_{15}H_{22}IN_3O_2$ requires: C, 44.7; H, 5.5; N, 10.4%.) Mp 108 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.98 (2H, s, Ph), 3.52 (4H, q, *J* 7.1, 2×NCH_2CH$_3$), 3.30 (4H, q, *J* 7.1, 2×NCH_2CH$_3$), 1.23 (6H, t, *J* 7.1, 2×NCH$_2$CH_3), 1.13 (6H, t, *J* 7.1, 2×NCH$_2$CH_3). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 166.5, 153.7, 132.9, 106.8, 43.3, 40.2, 14.2, 12.7.

4.2.6. 4-(Trimethylsilylethynyl)-2,6-bis(diethylcarbamoyl)-pyridine (*7*)

Prepared according to general procedure A with 4-iodo-2,6-bis(diethylcarbamoyl)pyridine: 2.0 g, 4.96 mmol, 1 equiv; THF: 80 mL; Et_3N: 80 mL; trimethylsilylacetylene: 1.05 mL, 7.44 mmol, 1.5 equiv; copper iodide: 151 mg, 0.79 mmol, 0.16 equiv; $Pd(PPh_3)_2Cl_2$: 278 mg, 0.40 mmol, 0.08 equiv; temperature: 25 °C; time: 96 h; chromatography: ethyl acetate; product: light brown solid (1.71 g, 92%). (Found: C, 64.5; H,

8.5; N, 11.3. $C_{20}H_{31}N_3O_2Si$ requires: C, 64.3; H, 8.4; N, 11.3%.) δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.58 (2H, s, Ph), 3.51 (4H, q, *J* 7.1, 2×NCH_2CH$_3$), 3.28 (4H, q, *J* 7.1, 2×NCH_2CH$_3$), 1.21 (6H, t, *J* 7.1, 2×NCH$_2$CH_3), 1.10 (6H, t, *J* 7.1, 2×NCH$_2$CH_3), 0.22 (9H, s, Si(CH_3)$_3$). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 167.5, 153.7, 133.5, 125.7, 101.9, 101.1, 43.2, 40.1, 14.2, 12.7, −0.45.

*4.2.7. 4-Ethynyl-2,6-bis(diethylcarbamoyl)pyridine (**8**)*

K_2CO_3 of 370 mg (2.68 mmol, 2 equiv) is added to a solution of 4-(trimethylsilylethynyl)-2,6-bis(diethylcarbamoyl)pyridine (500 mg, 1.34 mmol, 1 equiv) in CH_2Cl_2/methanol (30 mL, 1:2). The mixture is stirred at room temperature for 1.5 h and 30 mL of water is added. The aqueous phase is extracted with CH_2Cl_2 (2×40 mL), and the organic phases are combined, washed with water (50 mL), brine (50 mL), and dried over Na_2SO_4. CH_2Cl_2 is evaporated under vacuum and the crude light brown solid is purified by flash chromatography with ethyl acetate to give our product as a light yellow solid (380 mg, 94%). (Found: C, 67.51; H, 7.76; N, 13.77. $C_{17}H_{23}N_3O_2$ requires: C, 67.75; H, 7.69; N, 13.94%.) Mp 116 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.63 (2H, s, Ph), 3.52 (4H, q, *J* 7.1, 2×NCH_2CH$_3$), 3.35 (1H, s, CC*H*), 3.29 (4H, q, *J* 7.1, 2×NCH_2CH$_3$), 1.22 (6H, t, *J* 7.1, 2×NCH$_2$CH_3), 1.12 (6H, t, *J* 7.1, 2×NCH$_2$CH_3). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 167.3, 153.8, 132.6, 126.0, 83.4, 80.1, 43.2, 40.2, 14.2, 12.7.

*4.2.8. 2-Acetyl-7-bromo-9,9-di-n-hexylfluorene (**10**)*

Acetyl chloride of 1.8 mL (25.4 mmol, 1.05 equiv) is slowly added at 0 °C to a suspension of anhydrous $AlCl_3$ (3.87 g, 29.0 mmol, 1.2 equiv) in dry CH_2Cl_2 (50 mL). A solution of 2-bromo-9,9-di-*n*-hexylfluorene (10.0 g, 24.2 mmol, 1 equiv) in dry CH_2Cl_2 (30 mL) is added drop by drop and the mixture is stirred at room temperature for 20 h. The mixture is poured onto 40 g of ice and a solution of concd HCl is added until the precipitate of $Al(OH)_3$ dissolves. The organic layer is separated and the aqueous phase is extracted twice with CH_2Cl_2. (2× 50 mL). The organic phases are combined, washed with water (50 mL), 2% NaOH solution (50 mL), water (50 mL), brine (50 mL), and dried over Na_2SO_4. After evaporation of the solvents, the yellow oil obtained is purified by flash chromatography (pentane/CH_2Cl_2, 2:1) to give the product as a colorless oil (10.25 g, 93%). (Found: C, 71.10; H, 7.87. $C_{27}H_{35}BrO$ requires: C, 71.20; H, 7.74%.) δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.90−7.96 (2H, m, Ph), 7.69 (1H, d, *J* 8.3, Ph), 7.58 (1H, d, *J* 7.8, Ph), 7.48 (1H, s, Ph), 7.46(2H, d, *J* 7.8, Ph), 2.63 (3H, s, COCH_3), 2.02−1.90 (4H, m, 2×CCH_2), 1.12−0.99 (12H, m, 2×CH_2CH_2-CH_2CH$_3$), 0.73 (6H, t, *J* 6.7, 2×CH$_2$CH_3), 0.61−0.48 (4H, m, 2×CCH$_2$CH_2). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 197.4, 153.7, 150.2, 144.4, 138.3, 135.7, 129.8, 127.8, 125.9, 122.2, 121.9, 121.5, 119.1, 55.2, 39.6, 30.9, 29.0, 26.3, 23.2, 22.0, 13.5.

*4.2.9. 7-Bromo-9,9-di-n-hexylfluoren-2-yl acetate (**11**)*

m-CPBA of 6 g (77%, 26.8 mmol, 1.6 equiv) is slowly added to a solution of 2-acetyl-7-bromo-9,9-di-*n*-hexylfluorene (7.5 g, 16.5 mmol, 1 equiv) in $CHCl_3$ (150 mL). The mixture is stirred in the dark at room temperature for 4 days, washed with $NaHCO_3$ (100 mL), water (100 mL), brine (100 mL), and dried over Na_2SO_4. After evaporation of the solvents and purification by flash chromatography (pentane/CH_2Cl_2, 1:2) the product is obtained as a light orange solid (6.35 g, 82%). (Found: C, 66.76; H, 7.30. $C_{27}H_{35}BrO_2 \cdot 1/4CH_2Cl_2$ requires: C, 66.43; H, 7.26%.) Mp 42 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.63 (1H, d, *J* 8.9, Ph), 7.56−7.34 (3H, m, Ph), 7.10−7.02 (2H, m, Ph), 2.31 (3H, s, COCH_3), 1.96−1.82 (4H, m, 2×CCH_2), 1.20−0.96 (12H, m, 2×CH_2CH_2CH_2CH$_3$), 0.76 (6H, t, *J* 6.6, 2×CH$_2$-CH_3), 0.70−0.56 (4H, m, 2×CCH$_2$CH_2). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 169.4, 153.1, 151.9, 150.5, 139.4, 137.7, 130.1, 126.2, 121.03, 120.99, 120.4, 120.3 116.4, 55.6, 40.3, 31.5, 29.7, 23.7, 22.6, 21.2, 14.0.

*4.2.10. 7-Bromo-9,9-di-n-hexylfluoren-2-ol (**12**)*

KOH of 4.2 g (75 mmol, 10 equiv) is added to a solution of 3.54 g of 7-bromo-9,9-di-*n*-hexylfluoren-2-yl acetate (7.5 mmol, 1 equiv) in water/ethanol (40 mL, 1:1). The mixture is stirred at 80 °C for 20 h. After cooling to room temperature, the reaction mixture is neutralized by the addition of a solution of concd HCl and extracted twice with diethyl ether (2×50 mL). The organic phases are combined, washed with water (50 mL), brine (50 mL), and dried over Na_2SO_4. After evaporation of the solvents, the yellow oil obtained is purified by flash chromatography (pentane/CH_2Cl_2, 1:4) to give the product as a white solid (3.22 g, 97%). (Found: C, 68.71; H, 7.63. $C_{25}H_{33}BrO \cdot 1/2H_2O$ requires: C, 68.49; H, 7.82%.) Mp 106 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.56−7.42 (2H, m, Ph), 7.42−7.34 (2H, m, Ph), 6.84−6.72 (2H, m, Ph), 1.92−1.80 (4H, m, 2×CCH_2), 1.22−0.94 (12H, m, 2×CH_2CH_2CH_2CH$_3$), 0.75 (6H, t, *J* 6.9, 2×CH$_2$CH_3), 0.74−0.54 (4H, m, 2×CCH$_2$CH_2). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 155.6, 152.8, 152.4, 140.0, 133.3, 129.9, 126.0, 120.8, 120.2, 119.8, 114.2, 110.1, 55.3, 40.5, 31.5, 29.7, 23.7, 22.6, 14.0.

*4.2.11. 2-n-Hexyloxy-7-bromo-9,9-di-n-hexylfluorene (**13**)*

To a solution of 7-bromo-9,9-di-*n*-hexylfluoren-2-ol (1.25 g, 2.92 mmol, 1 equiv) and 1-bromohexane (0.45 mL, 3.21 mmol, 1.1 equiv) in acetonitrile (20 mL) is added K_2CO_3 (805 mg, 5.82 mmol, 2 equiv). The mixture is stirred at 82 °C for 20 h. After cooling to room temperature, the mixture is added to distilled water (40 mL) and extracted with diethyl ether (3×40 mL). The organic phases are combined, washed with water (50 mL), brine (50 mL), and dried over Na_2SO_4. After evaporation of the solvents and purification by flash chromatography (pentane/CH_2Cl_2, 1:4), the product is obtained as a white solid (1.27 g, 85%). (Found: C, 72.69; H, 8.77. $C_{31}H_{45}BrO$ requires: C, 72.50; H, 8.83%.) Mp 39 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.56−7.35 (4H, m, Ph), 6.90−6.76 (2H, m, Ph), 3.99 (2H, m, OCH_2), 1.93−1.70 (6H, m, OCH$_2$CH_2+2×CCH_2), 1.58−1.26 (6H, m, OCH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 1.20−0.95 (12H, m, 2×CH_2CH_2CH_2CH$_3$), 0.89 (3H, t, *J* 6.9, OCH$_2$CH$_2$CH$_2$CH$_2$-CH_2CH_3), 0.71 (6H, t, *J* 6.9, 2×CH$_2$CH_3), 0.68−0.50 (4H, m, 2×CCH$_2$CH_2). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 159.5, 152.5, 152.3, 140.3, 133.0, 129.8, 126.0, 120.5, 120.2, 119.7, 113.0, 109.5, 68.4, 55.4, 40.5, 31.7, 31.5, 29.7, 29.4, 25.9, 23.7, 22.7, 22.6, 14.1, 14.0.

*4.2.12. 2-(7-Hexyloxy-9,9′-dihexylfluorenyl)trimethylsilylacetylene (**14**)*

Prepared according to general procedure A with 2-hexyloxy-7-bromo-9,9-di-*n*-hexylfluorene: 606 mg, 1.18 mmol, 1 equiv; DMF: 14 mL; Et_3N: 1.64 mL, 11.8 mmol, 10 equiv; trimethylsilylacetylene: 1.67 mL, 11.8 mmol, 10 equiv; copper iodide: 44.8 mg, 0.236 mmol, 0.2 equiv; $Pd(PPh_3)_2Cl_2$: 82.8 mg, 0.118 mmol, 0.1 equiv; temperature: 115 °C; time: 3 days; chromatography: pentane; product: yellow oil (520 mg, 84%). (Found: C, 81.11; H, 10.01. $C_{36}H_{54}OSi$ requires: C, 81.44; H, 10.25%.) δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.59–7.38 (4H, m, Ph), 6.90–6.82 (2H, m, Ph), 3.99 (2H, m, OCH_2), 1.95–1.72 (6H, m, OCH_2CH_2+2×CCH_2), 1.58–1.26 (6H, m, OCH_2CH_2-$CH_2CH_2CH_2CH_3$), 1.20–0.95 (12H, m, 2×$CH_2CH_2CH_2CH_2CH_3$), 0.90 (3H, t, *J* 6.9, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 0.75 (6H, t, *J* 7.0, 2×CH_2CH_3), 0.68–0.50 (4H, m, 2×CCH_2CH_2), 0.27 (9H, s, $Si(CH_3)_3$). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 159.5, 153.1, 150.1, 141.8, 133.3, 131.2, 126.1, 120.8, 119.9, 118.6, 113.0, 109.4, 106.6, 93.3, 77.2, 68.4, 55.1, 40.6, 31.7, 31.6, 29.7, 29.4, 25.8, 23.6, 22.6, 14.1, 14.0, −0.1.

*4.2.13. 2-(7-Hexyloxy-9,9′-dihexylfluorenyl)acetylene (**15**)*

K_2CO_3 of 285 mg (2.05 mmol, 2.6 equiv) is added to a solution of 2-(7-hexyloxy-9,9′-dihexylfluorenyl)trimethylsilylacetylene (420 mg, 0.8 mmol, 1 equiv) in THF/methanol (20 mL, 1:1). The mixture is stirred at room temperature for 3 h and 30 mL of pentane is added. The remaining K_2CO_3 is filtered, and after evaporation of the solvents and purification by flash chromatography (pentane/CH_2Cl_2, 1:9), the product is obtained as a yellow oil (0.355 g, 95%). (Found: C, 86.22; H, 9.88. $C_{33}H_{46}O$ requires: C, 86.40; H, 10.11%.) δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.65–7.35 (4H, m, Ph), 6.90–6.81 (2H, m, Ph), 3.99 (2H, m, OCH_2), 3.08 (1H, s, CCH), 1.98–1.76 (6H, m, OCH_2CH_2+2×CCH_2), 1.58–1.26 (6H, m, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 1.20–0.95 (12H, m, 2×$CH_2CH_2CH_2CH_2CH_3$), 0.89 (3H, t, *J* 6.9, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 0.74 (6H, t, *J* 7.0, 2×CH_2CH_3), 0.68–0.51 (4H, m, 2×CCH_2CH_2). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 159.6, 153.1, 150.2, 142.1, 133.2, 131.2, 126.3, 120.8, 118.8, 118.7, 113.1, 109.4, 85.0, 77.2, 76.5, 68.4, 55.1, 40.5, 31.7, 31.5, 29.7, 29.4, 25.8, 23.6, 22.6, 14.1, 14.

*4.2.14. 2-Iodo-7-nitro-9,9-di-n-hexylfluorene (**16**)*

A 50% aqueous solution of NaOH (3.8 mL, 72.4 mmol, 7 equiv) is added under argon to a solution of 2-iodo-7-nitrofluorene (3.5 g, 10.4 mmol, 1 equiv) and triethylbenzylammonium chloride (130 mg, 0.57 mmol, 0.055 equiv) in DMSO (35 mL). Once the mixture becomes dark green, 4.39 mL of 1-bromohexane (31.2 mmol, 3 equiv) is added drop by drop and the mixture is stirred at room temperature for 20 h. An excess of ethyl acetate is added (50 mL) and the organic layer is filtered, washed with 10 M HCl (50 mL), water (50 mL), brine (50 mL), and dried over Na_2SO_4. After evaporation of the solvents, the crude red oil is purified by chromatography (pentane/CH_2Cl_2, 6:1) to give product as a light yellow solid (4.77 g, 91%). (Found: C, 59.44; H, 6.43; N, 2.80. $C_{25}H_{32}INO_2$ requires: C, 59.41; H, 6.18; N, 2.77%.) Mp 65 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 8.24 (1H, dd, *J* 8.3 and 2.1, Ph), 8.16 (1H, d, *J* 1.9, Ph), 7.77–7.69 (3H, m, Ph) 7.50 (1H, d, *J* 8.3, Ph), 2.03–1.92 (4H, m, 2×CCH_2), 1.11–1.03 (12H, m, 2×$CH_2CH_2CH_2CH_3$), 0.75 (6H, t, *J* 6.2, 2×CH_2CH_3), 0.58–0.51 (4H, m, 2×CCH_2-CH_2). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 154.5, 151.4, 147.5, 146.5, 138.3, 136.6, 132.5, 123.4, 122.7, 120.0, 118.2, 95.5, 55.9, 39.9, 31.4, 29.45, 23.7, 22.5, 13.9.

*4.2.15. 2-Amino-7-iodo-9,9-di-n-hexylfluorene (**17**)*

A mixture of 2-nitro-7-iodo-9,9-di-*n*-hexylfluorene (5.55 g, 11.0 mmol, 1 equiv) and iron powder (Aldrich-325 mesh, 3.07 g, 54.9 mmol, 5 equiv) in glacial acetic acid (130 mL) is heated to boiling. The heat is stopped and, once the boiling stops, more iron powder (Aldrich-325 mesh, 1.23 g, 21.96 mmol, 2 equiv) is added. The mixture is first stirred at 118 °C for 30 min, then cooled down to room temperature, and added to 10 mL distilled water. The mixture is sonicated for 10 min and filtered. The brown solid obtained is washed with water and dissolved in CH_2Cl_2. This solution is then washed with water, saturated aqueous $NaHCO_3$, brine, dried over Na_2SO_4, and evaporated under vacuum. The crude yellow solid is purified by chromatography (pentane/ethyl acetate, 4:1) to give the product as a light brown solid (3.60 mg, 69%.) (Found: C, 63.07; H, 7.35; N, 2.75. $C_{25}H_{34}IN$ requires: C, 63.15; H, 7.21; N, 2.95%.) Mp 39 °C. δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.58–7.55 (2H, m, Ph), 7.41 (1H, d, *J* 8.6, Ph), 7.27 (1H, d, *J* 8.4, Ph), 6.64–6.60 (2H, m, Ph), 3.76 (2H, s, NH_2), 1.86 (4H, t, *J* 8.2, 2×CCH_2), 1.25–1.06 (12H, m, 2×$CH_2CH_2CH_2CH_3$), 0.78 (6H, t, *J* 6.2, 2×CH_2CH_3), 0.65–0.53 (4H, m, 2×CCH_2CH_2). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 152.3, 152.16, 146.56, 141.3, 135.6, 131.7, 131.3, 120.7, 120.1, 114.0, 109.5, 90.2, 55.0, 40.5, 31.5, 29.7, 23.7, 22.6, 14.1.

*4.2.16. N,N-Dihexyl-2-amino-7-iodo-9,9-di-n-hexylfluorene (**18**)*

To a solution of 2-amino-7-iodo-9,9-di-*n*-hexylfluorene (1.66 g, 3.49 mmol, 1 equiv), 1-bromohexane (1.97 mL, 13.97 mmol, 4 equiv), and sodium iodide (2.09 g, 13.97 mmol, 4 equiv) in dry DMF (18 mL) is added Na_2CO_3 (666 mg, 6.28 mmol, 1.8 equiv). The mixture is stirred at 95 °C for 20 h. After cooling to room temperature, the mixture is added to distilled water (40 mL) and extracted with diethyl ether (3×40 mL). The organic layers are combined, washed with water (50 mL), brine (50 mL), and dried over Na_2SO_4. After evaporation of the solvents, the brown oil obtained is purified by flash chromatography (pentane/CH_2Cl_2, 9:1) to give the product as a light yellow oil (1.6 g, 71%). (Found: C, 68.78; H, 9.32; N, 2.27. $C_{37}H_{58}IN$ requires: C, 69.03; H, 9.08; N, 2.18%.) δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.55–7.51 (2H, m, Ph), 7.44 (1H, d, *J* 8.4, Ph), 7.24 (1H, d, *J* 7.3, Ph), 6.58 (1H, d, *J* 8.4, Ph), 6.53 (1H, m, Ph), 3.30 (4H, t, *J* 7.5, 2×NCH_2), 1.88–1.80 (4H, m, 2×NCH_2CH_2), 1.60–1.51 (4H, m, 2×CCH_2), 1.39–1.23 (12H, m, 2×$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.12–0.99 (12H, m, 2×$CCH_2CH_2CH_2CH_2CH_2CH_3$), 0.88 (6H, t, *J* 6.8, 2×$NCH_2CH_2CH_2CH_2CH_2CH_3$), 0.78 (6H, t, *J* 6.2, 2×$CCH_2CH_2CH_2CH_2CH_2CH_3$), 0.72–0.60 (4H, m, 2×$CCH_2CH_2$). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 152.4, 151.8, 148.5, 141.7,

135.5, 131.5, 138.0, 120.5, 119.7, 110.8, 106.1, 89.1, 55.0, 51.5, 40.5, 31.8, 31.5, 29.7, 27.2, 26.9, 23.7, 22.65, 22.60, 14.03, 14.01.

4.2.17. N,N-Bis(4-(diethylamino)phenyl)pyridine-2,6-dicarboxamide (**L^{1}**)

The procedure for the synthesis of **L$^{1'}$** was used. *p*-*N*,*N*-diethylaminoaniline: 5.01 g, 30.5 mmol, 5 equiv; pyridine-2,6-dicarbonyl dichloride: 1.25 g, 6.1 mmol, 1 equiv; product: light green crystals (2.4 g, 90%). λ_{max} (CH_2Cl_2)/nm 360 (ε/dm^3 mol^{-1} cm^{-1} 13,900). ν_{max}/cm^{-1} 1670 (CO). δ_H (200 MHz, $CDCl_3$, Me_4Si) 9.62 (2H, s, 2×N*H*), 8.40 (2H, d, *J* 7.6, Ph), 8.06 (1H, t, *J* 7.6, Ph), 7.55 (4H, d, *J* 8.8, Ph), 6.64 (4H, d, *J* 8.8, Ph), 3.36 (8H, q, *J* 7.0, 4×NC*H*$_2$), 1.18 (12H, t, *J* 7.0, 4×C*H*$_3$). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 161.5, 149.7, 145.8, 139.4, 126.2, 125.1, 123.0, 112.2, 44.8, 12.8. *m*/*z* 498.2248 (MK^+. $C_{27}H_{33}KN_5O_2$ requires 498.2271).

4.2.18. N,N-Bis(4-(dibutylamino)phenyl)pyridine-2,6-dicarboxamide (**L$^{1'}$**)

p-*N*,*N*-Dibutylaminoaniline of 6.0 g (27.2 mmol, 5 equiv) is added to a 10 mL CH_2Cl_2 solution of pyridine-2,6-dicarbonyl dichloride prepared in situ (1.11 g, 5.45 mmol, 1 equiv, see preparation of **5**). After stirring at 40 °C for 2 h, the acidic mixture is quenched to neutral pH by the addition of a saturated aqueous solution of K_2CO_3. After extraction, the organic phase is dried (Na_2SO_4) and evaporated. The crude product is recrystallized twice from heptane to give 1.9 g (61%) of light green crystals. (Found: C, 60.08; H, 7.61; N, 8.85. $C_{35}H_{49}N_5O_2\cdot 2CH_2Cl_2$ requires: C, 59.92; H, 7.20; N, 9.44%.) λ_{max} (CH_2Cl_2)/nm 360 (ε/dm^3 mol^{-1} cm^{-1} 13,900). ν_{max}/cm^{-1} 1671 (CO). δ_H (200 MHz, $CDCl_3$, Me_4Si) 9.40 (2H, s, 2×N*H*), 8.46 (2H, d, *J* 7.7, Ph), 8.10 (1H, t, *J* 7.7, Ph), 7.58 (4H, d, *J* 8.9, Ph), 6.68 (4H, d, *J* 8.9, Ph), 3.29 (8H, t, *J* 7.1, 4×NC*H*$_2$), 1.67–1.56 (16H, m, 4×NCH$_2$C*H*$_2$C*H*$_2$), 0.98 (12H, t, *J* 7.1, 4×C*H*$_3$). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 160.9, 149.4, 145.9, 139.1, 125.6, 124.2, 122.3, 111.7, 52.8, 29.4, 20.3 13.8. *m*/*z* 610.3526 (MK^+. $C_{35}H_{49}KN_5O_2$ requires 610.3523).

4.2.19. 4-(4-(Hexyloxyphenyl)acetylene)-2,6-di(diethylcarbamoyl)pyridine (**L^{2}**)

Prepared according to general procedure A with 4-iodo-2,6-di(diethylcarbamoyl)pyridine: 1.5 g, 3.7 mmol, 1 equiv; THF: 20 mL; Et_3N: 20 mL; 4-(hexyloxy)phenylacetylene: 830 mg, 4.1 mmol, 1.1 equiv; copper iodide: 140 mg, 0.74 mmol, 0.2 equiv; $Pd(PPh_3)_2Cl_2$: 260 mg, 0.37 mmol, 0.1 equiv; temperature: 40 °C; time: 72 h; chromatography: gradient pentane/ethyl acetate from 9:1 to 1:1; product: pale yellow solid (1.576 g, 89%). (Found: C, 72.93; H, 8.29; N, 8.27. $C_{29}H_{39}N_3O_3$ requires: C, 72.92; H, 8.23; N, 8.80%.) Mp 84 °C. λ_{max} (CH_2Cl_2)/nm 320 (ε/dm^3 mol^{-1} cm^{-1} 28,600). ν_{max}/cm^{-1} 2202 (CC), 1624 (CO). δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.59 (2H, s, Ph), 7.51 (2H, d, *J* 8.9, Ph), 6.94 (2H, t, *J* 8.9, Ph), 4.00 (2H, t, *J* 6.5, OC*H*$_2$), 3.48 (4H, q, *J* 7.1, 2×NC*H*$_2$), 3.25 (4H, q, *J* 7.1, 2×NC*H*$_2$), 1.74 (2H, m, OCH$_2$C*H*$_2$), 1.35 (6H, m, OCH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_2$), 1.18 (6H, t, *J* 7.1, 2×NCH$_2$C*H*$_3$), 1.08 (6H, t, *J* 7.1, 2×NCH$_2$C*H*$_3$), 0.89 (3H, *J* 7.1, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 166.8, 159.9, 154.2, 133.13, 133.15, 123.2, 114.4, 112.7, 95.0, 84.4, 67.6, 42.4, 39.0, 30.8, 28.3, 24.8, 21.8, 13.1, 12.8, 11.6. *m*/*z* 500.2894 (MNa^+. $C_{29}H_{39}NaN_3O_3$ requires 500.2889).

4.2.20. Dimethyl 4-((4-hexyloxyphenyl)ethynyl)pyridine-2,6-dicarboxylate (**L$^{2'}$**)

Prepared according to general procedure A with, *experiment* 1: dimethyl 4-bromopyridine-2,6-dicarboxylate: 1.0 g, 3.65 mmol, 1 equiv; THF: 20 mL; Et_3N: 5 mL; 4-(hexyloxy)-phenylacetylene: 738 mg, 3.65 mmol, 1 equiv; copper iodide: 69.5 mg, 0.365 mmol, 0.1 equiv; $Pd(PPh_3)_2Cl_2$: 128.1 mg, 0.183 mmol, 0.05 equiv; temperature: 66 °C; time: 20 h; chromatography: pure CH_2Cl_2 followed by CH_2Cl_2/ethyl acetate from 4:1; product: white solid (600 mg, 45%). *Experiment* 2: dimethyl 4-iodopyridine-2,6-dicarboxylate: 1.17 g, 3.65 mmol, 1 equiv; THF: 20 mL; Et_3N: 5 mL; 4-(hexyloxy)phenylacetylene: 738 mg, 3.65 mmol, 1 equiv; copper iodide: 69.5 mg, 0.365 mmol, 0.1 equiv; $Pd(PPh_3)_2Cl_2$: 128.1 mg, 0.183 mmol, 0.05 equiv; temperature: 40 °C; time: 5 h; product recrystallized from methanol: white solid (1.24 g, 93%). (Found: C, 69.90; H, 6.41; N, 3.28. $C_{23}H_{25}NO_5$ requires: C, 69.86; H, 6.37; N, 3.54%.) Mp 117 °C. λ_{max} (CH_2Cl_2)/nm 336 (ε/dm^3 mol^{-1} cm^{-1} 20,400). ν_{max}/cm^{-1} 2216 (CC), 1720 (CO). δ_H (200 MHz, $CDCl_3$, Me_4Si) 8.35 (2H, s, Ph), 7.52 (2H, d, *J* 8.9, Ph), 6.92 (2H, d, *J* 8.9, Ph), 4.06 (6H, s, COOC*H*$_3$), 4.01 (2H, t, *J* 6.5, OC*H*$_2$), 1.90–1.70 (2H, m, OCH$_2$C*H*$_2$), 1.55–1.30 (6H, m, OCH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$), 0.95 (3H, t, *J* 6.6, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 165.2, 160.9, 148.7, 135.4, 134.3, 129.8, 115.1, 113.4, 98.1, 85.0, 68.6, 53.7, 32.0, 29.5, 26.1, 23.0, 14.1.

4.2.21. 4-((4-Hexyloxyphenyl)ethynyl)pyridine-2,6-dicarboxylic acid (**L$^{2''}$**)

Dimethyl 4-((4-hexyloxyphenyl)ethynyl)pyridine-2,6-dicarboxylate of 500 mg (1.26 mmol, 1 equiv) is added to a solution of sodium hydroxide (151 mg, 3.78 mmol, 3 equiv) in water/methanol (15 mL, 19:1). After stirring at 100 °C for 15 h, the solution is cooled down to room temperature and is acidified to pH=2 by the addition of a 1 mol L^{-1} HCl solution. The precipitate obtained is filtered, washed with water, triturated with pentane, and dried under vacuum to give 510 mg (99%) of a white solid. (Found: C, 60.65; H, 5,72; N, 3.11. $C_{21}H_{21}NO_5\cdot H_2O\cdot HCl$ requires: C, 59.79; H, 5.54; N, 3.32%.) λ_{max} (CH_2Cl_2)/nm 346 (ε/dm^3 mol^{-1} cm^{-1} 25,700). ν_{max}/cm^{-1} 2231 (CC), 1743 (CO). δ_H (200 MHz, $CDCl_3$, Me_4Si) 8.14 (2H, s, Ph), 7.61 (2H, d, *J* 8.7, Ph), 7.02 (2H, d, *J* 8.7, Ph), 4.03 (2H, t, *J* 6.4, OC*H*$_2$), 1.80–1.60 (2H, m, OCH$_2$C*H*$_2$), 1.50–1.20 (6H, m, OCH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_2$), 0.88 (3H, t, *J* 5.8, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 165.8, 160.4, 151.1, 134.3, 133.5, 127.6, 115.5, 113.3, 96.5, 85.7, 68.2, 31.4, 29.0, 25.6, 22.5, 14.4.

*4.2.22. 4-(N,N-Dihexyl-4-ethynylaniline)-2,6-di(diethylcarbamoyl)pyridine (**L**^{3})*

Prepared according to general procedure A with 4-iodo-2,6-di(diethylcarbamoyl)pyridine: 1.298 g, 3.2 mmol, 1 equiv; THF: 20 mL; Et_3N: 20 mL; *N*,*N*-dihexyl-4-ethynylaniline: 1.029 g, 3.5 mmol, 1.1 equiv; copper iodide: 136 mg, 0.7 mmol, 0.2 equiv; $Pd(PPh_3)_2Cl_2$: 251 mg, 0.3 mmol, 0.09 equiv; temperature: 40 °C; time: 72 h; chromatography: gradient pentane/ethyl acetate from 4:1 to 2:1; product: orange solid (982 mg, 53%). (Found: C, 75.04; H, 9.38; N, 9.78. $C_{35}H_{52}N_4O_2$ requires: C, 74.96; H, 9.35; N, 9.99%.) Mp 101 °C. λ_{max} (CH_2Cl_2)/nm 379 (ε/dm^3 mol^{-1} cm^{-1} 40,800). ν_{max}/cm^{-1} 2203 (CC), 1625 (CO). δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.47 (2H, s, Ph), 7.35 (2H, d, *J* 9.0, Ph), 6.64 (2H, d, *J* 9.0, Ph), 3.48 (4H, q, *J* 7.2, 2×CONCH_2), 3.60–3.30 (8H, m, 2×CONCH_2+2×NCH_2), 1.70–1.45 (4H, m, 2×NCH$_2$CH_2), 145–1.20 (12H, m, 2×NCH$_2$CH$_2$CH_2CH$_2$CH_2), 1.18 (6H, t, *J* 7.2, 2×NCH$_2$CH_3), 1.08 (6H, t, *J* 7.2, 2×NCH$_2$CH_3), 0.88 (3H, t, *J* 6.4, 2×NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 166.9, 154.2, 148.6, 133.8, 132.9, 122.2, 110.9, 105.7, 97.4, 84.0, 49.9, 42.4, 39.0, 30.9, 26.3, 25.8, 21.9, 13.1, 12.8, 11.6.

*4.2.23. 4-(2-(7-Hexyloxy-9,9′-dihexylfluorenyl)ethynyl)-2,6-di(diethylcarbamoyl)pyridine (**L**^{4})*

Prepared according to general procedure A with 4-iodo-2,6-di(diethylcarbamoyl)pyridine: 271 mg, 0.672 mmol, 1 equiv; THF: 20 mL; Et_3N: 10 mL; 2-(7-hexyloxy-9,9′-dihexylfluorenyl)acetylene: 308 mg, 0.672 mmol, 1 equiv; copper iodide: 25.5 mg, 0.134 mmol, 0.2 equiv; $Pd(PPh_3)_2Cl_2$: 47.2 mg, 0.0672 mmol, 0.1 equiv; temperature: 50 °C; time: 20 h; chromatography: pentane/ethyl acetate (2:1); product: pale yellow solid (320 mg, 65%). (Found: C, 78.49; H, 9.25; N, 5.54. $C_{48}H_{67}N_3O_3$ requires: C, 78.54; H, 9.20; N, 5.72%.) Mp 130 °C. λ_{max} (CH_2Cl_2)/nm 349 (ε/dm^3 mol^{-1} cm^{-1} 43,000). ν_{max}/cm^{-1} 2212 (CC), 1633 (CO). δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.67 (2H, s, Ph), 7.65–7.54 (2H, m, Ph), 7.48–7.42 (2H, m, Ph), 6.90–6.82 (2H, m, Ph), 4.00 (2H, t, *J* 6.6, OCH_2), 3.54 (4H, q, *J* 7.1, 2×NCH_2), 3.32 (4H, q, *J* 7.1, 2×NCH_2), 1.88 (6H, m, OCH$_2$CH_2+2×CCH_2), 1.44 (2H, m, CH_2), 1.34 (4H, m, 2×CH_2), 1.24 (6H, t, *J* 7.1, 2×NCH$_2$CH_3), 1.14 (6H, t, *J* 7.1, 2×NCH$_2$CH_3), 1.03 (12H, m, 6×CH_2), 0.90 (6H, t, *J* 6.8, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3), 0.74 (6H, t, *J* 7.1, 2×CCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3), 0.59 (4H, m, 2×CH_2). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 167.7, 159.8, 153.8, 153.3, 150.4, 142.9, 134.1, 133.0, 131.2, 126.2, 125.2, 121.1, 118.9, 118.5, 113.2, 109.4, 97.4, 86.0, 68.3, 55.2, 43.3, 40.5, 40.2, 31.7, 31.5, 29.7, 29.3, 25.8, 23.7, 22.61 22.60, 14.3, 14.1, 14.0, 12.8.

*4.2.24. 4-(2′-(N,N-Dihexyl-7′-amino-9′,9′-dihexylfluorene)-ethynyl)-2,6-bis(diethylcarbamoyl)pyridine (**L**^{5})*

Prepared according to general procedure A with *N*,*N*-dihexyl-2-amino-7-iodo-9,9-di-*n*-hexylfluorene: 641 mg, 0.995 mmol, 1 equiv; THF: 30 mL; Et_3N: 30 mL; 4-ethynyl-2,6-bis(diethylcarbamoyl)pyridine: 300 mg, 0.995 mmol, 1 equiv; copper iodide: 30 mg, 0.16 mmol, 0.16 equiv; $Pd(PPh_3)_2Cl_2$: 56 mg, 0.08 mmol, 0.08 equiv; temperature: 40 °C; time: 43 h; chromatography: pentane/ethyl acetate (2:1); product: yellow oil (430 mg, 59%). (Found: C, 76.49; H, 9.72; N, 6.26. $C_{54}H_{80}N_4O_2\cdot 2H_2O$ requires: C, 76.01; H, 9.92; N, 6.57%.) Mp 84 °C. λ_{max} (CH_2Cl_2)/nm 402 (ε/dm^3 mol^{-1} cm^{-1} 37,300). ν_{max}/cm^{-1} 2203 (CC), 1640 (CO). δ_H (200 MHz, $CDCl_3$, Me_4Si) 7.56 (2H, s, Ph), 7.55–7.45 (4H, m, Ph), 6.67–6.59 (2H, m, Ph), 3.49 (4H, q, *J* 7.1, 2×NCH_2), 3,32 (4H, q, *J* 7.3, 2×NCH_2), 3.27 (4H, q, *J* 7.1, 2×NCH_2), 1.58 (4H, m, 2×CCH_2), 1.40–1.90 (40H, m, 4×NCH$_2$CH_3+14×CH_2), 0.88 (6H, t, *J* 6.8, NCH$_2$CH$_2$CH$_2$-CH$_2$CH$_2$CH_3), 0.74 (6H, t, *J* 6.9, 2×CCH$_2$CH$_2$CH$_2$CH$_2$-CH$_2$CH_3), 0.55 (4H, m, 2×CH_2). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 167.7, 153.8, 153.1, 149.9, 148.7, 143.8, 134.3, 131.2, 128.0, 126.0, 125.1, 121.1, 117.9, 116.8, 110.9, 106.0, 98.0, 85.7, 54.8, 51.5, 43.3, 40.6, 40.1, 31.8, 31.5, 29.7, 27.2, 26.9, 23.7, 22.6 22.5, 14.3, 14.1, 14.0, 12.8.

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