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Syntheses of Uncharged, Positively and Negatively Charged 3,4,9,10-Perylene-Bis(Dicarboximides)

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ABSTRACT

The preparation of various 3,4,9,10-perylene-bis(dicarboximides) bearing uncharged, negatively and positively charged substituents on the imide group is described. The absorption and fluorescence bands are not influenced by the type of substituent, but in contrast, the fluorescence quantum yields of the compounds are different.

1 INTRODUCTION

Vat dyes and pigments based on imide substituted 3,4,9,10-perylene-bis(dicarboximides) (PTCDI) **2** are very lightfast and highly fluorescent. Besides their classical applications as dyes and pigments, these compounds are interesting as laser dyes, in fluorescent solar collectors, as fluorescent markers in medical applications,[1–3] *n*-conductors in organic solar cells,[4] O_2 sensors in optodes, and sensitizers in solution.[5–10] Ford *et al.*[11,12] reported on redox potentials, and Tsuchida *et al.*[13] about the epitaxial growth of PTCDIs on KCl. Yanagi *et al.*[14] reported an optimal design for photovoltaic properties of two-layer organic solar cells using phthalocyanines and perylene-derivatives.

Several papers describe the synthesis of PTCDIs by the reaction of perylene-3,4,9,10-tetracarboxylic acid anhydride (PTCDA) **1** with an appropriate amine or by alkali fusion from substituted naphthalimides.[1–3,15–22] In order to optimize the above mentioned properties, the

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synthesis of various PTCDI bearing different substituents at the imide group is necessary. This paper describes the preparations of various new substituted uncharged, positively and negatively charged PTCDIs; the compounds can exhibit good solubility in organic solvents or water. Fluorescence yields of some of the PTCDIs were also determined.

2 RESULTS

Three standard methods for the synthesis of PTCDIs have been described in the literature[1–3,15–22] and these were applied to the syntheses of **2a-h**.

Method I

PTCDA **1** was heated with the appropriate amine in the presence of dicyclohexylcarbodiimide (DCC) as water separating reagent at 220–240°C using a small amount of quinoline as solvent. Nearly quantitative yields (85–98%) of PTCDI **2a-f** were obtained after 18 h reaction time. The products were treated several times with methanol in order to remove quinoline, then with aqueous sodium carbonate to dissolve unreacted **1**, and finally recrystallized from toluene or dimethylformamide (DMF). For high purification, **2a-f** could be vacuum sublimed. Compounds **2a-f** exhibited solubility in organic solvents such as DMF, dimethylsulfoxide (DMSO) and methylene chloride. The solubility of **2a-f** increased from 10^{-5} to 10^{-4} M as follows: **2f** < **2e** < **2d** < **2c** < **2a** < **2b**.

Method II

The imides **2g** (n = 2,3,6) could not be obtained using Method I because the bifunctional amines react with the dianhydride **1** with formation of oligomeric polyimides. For the syntheses of **2g** (n = 2,3,6) a method described by Lukác and Langhals[19] was modified. PTCDA was reacted with a large excess of a bifunctional amine in boiling toluene (lower temperature in comparison with Method I). Unreacted **1** was removed with KOH and the oligomeric by-product formed was removed by dissolving **2g** (n = 2, 3, 6) in formic acid.

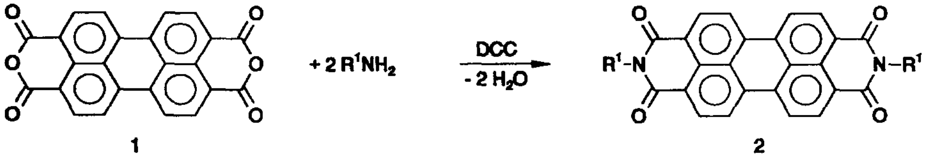
Method III

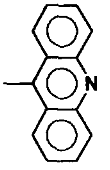
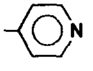
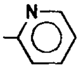
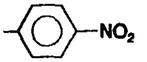
In order to prepare the bicarboxylates **2h** (n = 1, 2, 4, 5), methods I and II could not be applied, because under these reaction conditions decarboxylation reactions occurred and bis-alkyl substituted PTCDIs were obtained as reaction products. A method described by Ford[23] for **2h** (n = 1) was successfully employed for the synthesis of the different dicarboxylates **2h**; PTCDA was reacted with the amino carboxylic acid in aqueous alkaline DMSO.

The reactions of **1** with the various amines to give **2a-h** were monitored by IR spectroscopy. The products exhibited no absorption at $\sim$1775 cm^{-1} ($\text{—C=O}_{\text{anhydride}}$) for **1** and are characterized by an intense absorption for $\text{—C=O}_{\text{imide}}$ at $\sim$1690 cm^{-1}.

Compounds **2a-f** gave characteristic mass spectra. All diimides **2a-h**, irrespective of the kind of substituent, exhibited very similar absorption spectra (λ_{max} = 527 ± 1 nm) and fluorescence emission spectra (λ_{max} = 540 ± 3 nm).

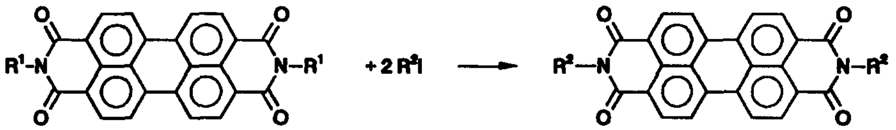
In order to increase the solubility of PTCDIs and to prepare positively charged PTCDIs, **2b-d** were alkylated in DMF using a tenfold excess of



diimide	R^1
2a	$-C_{16}H_{33}$
2b	$-CH_2CH_2CH_2N(CH_3)_2$
2c	
2d	
2e	
2f	
2g(n=2,3,6)	$-(CH_2)_n-NH_2$
2h(n=1,2,4,5)	$-(CH_2)_n-COO^-K^+$

different alkyliodides (CH_3I, $C_6H_{13}I$, $C_{12}H_{25}I$, $C_{16}H_{33}I$). All the alkylated diimides **3a-l** showed a good solubility in DMSO and DMF up to 10^{-3} mol l^{-1}. The diimides which were alkylated by methyliodide were also soluble in water, the solubility decreasing significantly with increasing chain length of the quarternizing alkyl groups.

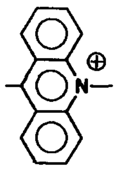
The structure of the products **3a-l** could only be evaluated using IR spectroscopy and elemental analysis; it was not possible to obtain ^1H NMR or mass spectra due to low solubility and low vapor pressure of the



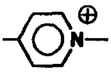
2 **3**

diimide	R^2
3a	$-CH_2CH_2CH_2N^+(CH_3)_2CH_3\ I^-$
3b	$-CH_2CH_2CH_2N^+(CH_3)_2C_6H_{13}\ I^-$
3c	$-CH_2CH_2CH_2N^+(CH_3)_2C_{12}H_{25}\ I^-$
3d	$-CH_2CH_2CH_2N^+(CH_3)_2C_{16}H_{33}\ I^-$
3e	Acrid-$CH_3\ I^-$
3f	Acrid-$C_6H_{13}\ I^-$
3g	Acrid-$C_{12}H_{25}\ I^-$
3h	Acrid-$C_{16}H_{33}\ I^-$
3i	Py-$CH_3\ I^-$
3j	Py-$C_6H_{13}\ I^-$
3k	Py-$C_{12}H_{25}\ I^-$
3l	Py-$C_{16}H_{33}\ I^-$

Acrid =



Py =



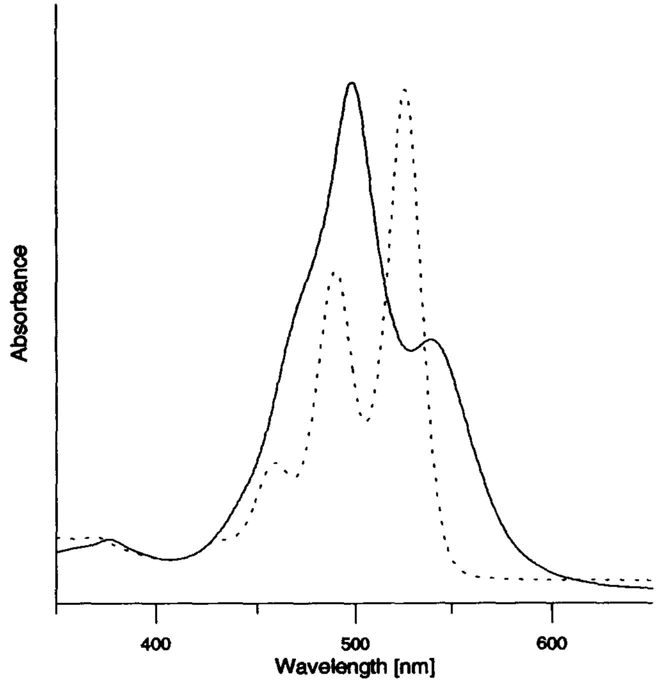


Fig. 1. Vis spectra of 10^{-5} M solutions of **3a** in water (- - - -) and in DMSO (———).

compounds. In concentrations necessary for ^{1}H NMR, the diimides **3a-l** showed a high degree of aggregation. The absorption maxima of all the diimides **3a-l** were at 528 ± 1 nm and the fluorescence maxima at 540 ± 3 nm. On increasing their concentration ($>10^{-6}$ mol l^{-1}), the diimides **3a-l** began to aggregate strongly; an example for the aggregation of **3a** is shown in Fig. 1. The maximum absorption for the aggregated diimides in the UV/vis-spectra shifted to shorter wavelength (from $\lambda \sim 525$ nm to $\lambda \sim 500$ nm) with a simultaneous decrease in the fluorescence quantum yield.

Fluorescence quantum yields were determined using 3,4,9,10-perylene-bis([2,5-di-*t*-butylphenyl]dicarboximide) (DPBI) in DMSO, with a quantum yield of nearly 100% as reference.[1,3,11,12] For this compound the same fluorescence intensities were observed under N_2 and air.

The diimides showed quantum yields in the range from 4 to 63%. All measurements for the quantum yields were carried out in DMSO (Table 1) or in aqueous alkaline micellar solution (Table 2) because the water soluble PTCDIs showed a very high tendency for aggregation, even when employing very low concentrations, as has been shown by Ford[23] for **2h** (n = 1). Oppositely charged detergents were added to the aqueous alkaline solutions of the ionic PTCDIs **3a**, **3b** and **2h** (n = 1, 2, 4, 5), namely

TABLE 1
Absorption, Fluorescence Emission and Quantum Yield Values (~10^{-5} mol l^{-1} in DMSO)

Diimide	E_{ab} *(nm)*	E_{fl} *(nm)*	ϕ_{fl} *(%)*
3a	526	537	28
3b	527	538	44
3c	526	538	41
3d	527	539	62
3e	527	538	26
3f	529	538	63
3g	527	539	62
3h	528	539	38
3i	528	538	20
3j	528	539	37
3k	528	543	27
3l	528	541	26

sodium dodecylsulphate (SDS) as negatively charged and cetyltrimethylammonium chloride (CTAC) as positively charged detergent. With oppositely charged detergents, total monomerization of the charged PTCDIs was achieved in aqueous solution. The neutral PTCDIs **2b** and **2g** (n = 2, 3, 6) could be dissolved (monomeric) in aqueous solution in the presence of SDS, whereas with CTAC aggregation was observed. The detergent concentration was always 0·05 M (a value which is known to be above the critical micellar concentration).

TABLE 2
Values of Quantum Yield (C_{PTCDI} ~ 10^{-5} mol l^{-1} in water with 0·06 M NaOH and 0·05 M detergent [SDS or CTAC]). λ_{ab} = 529 nm, λ_{ab} = 540 nm

Diimide	*Detergent*	ϕ_{fl} *(%)*
2g (n = 2)	SDS	27·0
2g (n = 3)	SDS	12·1
2g (n = 6)	SDS	4
2b	SDS	12·4
3a	SDS	47·3
3b	SDS	29·3
2h (n = 1)	CTAC	22·8
2h (n = 2)	CTAC	10·9
2h (n = 4)	CTAC	17
2h (n = 5)	CTAC	30·8

3 DISCUSSION

The various 3,4,9,10-perylene-bis(dicarboximides) bearing different hydrophobic, basic, negatively charged or positively charged substituents were prepared in high yields. These compounds are of interest in applications mentioned in the introduction. The variation in the nature of the substituents had no significant influence on the position of the absorption fluorescence bands. The uncharged diimides **2a-f** exhibited a low solubility in organic solvents, but a good stability against high temperatures (they could be purified by sublimation). The alkylated positively charged imides **3a-l** showed a better solubility in organic solvents in comparison with the uncharged **2**. In organic solvents, aggregation readily occurred at higher concentration. The charged PTCDIs **2h**, **3a-l** exhibited different aqueous solubility and were strongly aggregated in this solvent. These charged PTCDIs were monomerized in water by adding oppositely charged detergents.

In contrast to the constant position of fluorescence, quantum yields varied over a wide range (4–63%) indicating a great influence of the nature of the substituent. Measurements in DMSO showed that in most cases the quantum yields increased due to a shielding effect with increasing chain length of the alkylated PTCDIs **3**. In water, in the presence of a detergent in a micellar arrangement, the situation is different. In SDS, increasing chain length resulted in a decrease in ϕ_{Fl}, whereas in CTAC no clear pattern was seen. Detailed analysis of the location of the PTCDIs in the micelles is thus necessary in order to rationalise the observed differences.

4 EXPERIMENTAL

4.1 General

Electronic spectra were recorded on a Perkin-Elmer Lambda 2 UV/VIS or a Lambda 9 UV/VIS/NIR absorption spectrophotometer. For FT-IR spectra a Biorad FTS-7/SPC 3200 spectrometer was employed. Fluorescence spectra (under air) were recorded on a Perkin-Elmer LS 50 fluorescence spectrophotometer, mass spectra on a Varian CH7A (EI) or a Finnigan MAT 8222 (DCI$^{\pm}$) and NMR spectra on a Bruker WH360 (360 mHz). Elemental analyses were carried out by the Beller Microanalytical Laboratory (37004 Göttingen, Germany). The purity of all compounds was monitored by TLC (Al_2O_3 neutral with DMF or toluene/acetone 4 : 1, or Kieselgel with CH_2Cl_2). R_F values between 0·1 and 0·6 were obtained.

PTCDA and the other chemicals were obtained in the highest available purity from Roth, Merck or Aldrich and employed without further purification, if not noted otherwise.

4.2 Syntheses

4.2.1 General procedure for ***Method I****: synthesis of 3,4,9,10-perylene-bis(hexadecyl-carboximide)* ***2a****, 3,4,9,10-perylene-bis ([*N,N'*-dimethyltrimethylene]-carboximide)* ***2b****, 3,4,9,10-perylene-bis(acridyl-carboximide)* ***2c****, 3,4,9,10-perylene-bis(4-pyridyl-carboximide)* ***2d****, 3,4,9,10-perylene-bis(2-pyridyl-carboximide)* ***2e****, 3,4,9,10-perylene-bis([*p*-nitrophenyl]-carboximide)* ***2f***

A mixture of 0·1 mol PTCDA, 0·3 mol amine (hexadecyl-, *N,N'*-dimethyltrimethylenedi-, acridyl-, 4-pyridyl-, 2-pyridyl-, (4-nitrophenyl)-amine), 0·2 mol DCC and 5–10 ml twice distilled quinoline was heated to 220–240°C for 18 h under an inert gas. After cooling to room temperature, the mixture was diluted with 150 ml methanol, stirred for 30 min and allowed to stand for 4 h at −10°C. The dark red residues were separated by filtration and washed with methanol and ether. The crude diimides were treated with a 5% sodium carbonate solution in water for 30 min at 90–100°C and this procedure was continued until all the excess anhydride was removed. The products were then recrystallized from DMF, toluene or xylene; for high purification, the diimides were sublimed under high vacuum. Yields of 85–98% were obtained.

MS: **2a** (DCI^- [NH_3]): *m/z* (%) = 838 (100), 614 (12). **2b** (DCI^- [NH_3]): *m/z* (%) = 560 (100), 475 (60). **2c** (DCI^- [NH_3]): *m/z* (%) = 744 (10), 649 (100), 567 (15), 554 (54), 472 (42). **2d** (EI, 70 eV, 200°C): *m/z* (%) = 544 (18), 467 (100). **2e** (EI, 70 eV, 200°C): *m/z* (%) = 544 (60), 467 (100), 390 (98). **2f** (DCI^- [NH_3]): *m/z* (%) = 632 (100), 512 (17), 138 (55).

UV/vis: **2a-f** [DMSO]: λ (log ε) = 462 ± 1 (4·26–4·28), 490 ± 1 (4·69–4·70), 525 ± 1 (4·92–4·93) nm. **2b** [H_2O, 0·06 M NaOH, 0·05 M SDS]: λ (log ε) = 462 (4·18), 491 (4·6), 528 (4·76) nm.

Fluorescence: **2a-f** [DMSO]: λ = 540 ± 3 nm. **2b** [H_2O, 0·06 M NaOH, 0·05 M SDS]: λ = 539 nm.

IR: **2a** [KBr]: ν = 2927 (s), 2845 (m), 1696 (s), 1657 (s), 1592 (s), 1348 (m), 1251 (w), 1090 (w), 813 (w), 748 (w) cm^{-1}. **2b** [KBr]: ν = 3017 (m), 2959 (m), 1696 (s), 1650 (s), 1592 (s) cm^{-1}. **2c** [KBr]: ν = 1695 (s), 1560 (s), 1593 (s), 1346 (s) cm^{-1}. **2d** [KBr]: ν = 1698 (s), 1595 (s), 1591 (s), 1348 (s) cm^{-1}. **2e** [KBr]: ν = 1695 (s), 1657 (s), 1592 (s), 1350 (s), 1249 (m) cm^{-1}. **2f** [KBr]: ν = 1704 (s), 1674 (s), 1592 (s), 1578 (w), 1522 (s), 1431 (w), 1405 (w), 1340 (s), 1253 (m), 1176 (w), 1124 (w), 857 (w), 822 (m), 810 (m), 749 (m) cm^{-1}.

^1H NMR **2a** [$C_2D_2Cl_4$]: δ = 8·55 (8H, m, $\underline{H}_{arom.}$), 4·08 (4H, t, N–$\underline{CH_2}$–), 1·16 (56H, m, N–CH_2–($\underline{CH_2}$)$_{14}$–CH_3), 0·78 (6H, q, –$\underline{CH_3}$) ppm.

*4.2.2 General procedure for **Method II**: synthesis of 3,4,9,10-perylene-bis-([N,N'-2-aminoethyl]-carboximide) **2g** (n = 2), 3,4,9,10-perylene-bis-([N,N'-3-aminopropyl]-carboximide) **2g** (n = 3), 3,4,9,10-perylene-bis-([N,N'-6-aminohexyl]-carboximide) **2g** (n = 6)*

A mixture of 0·45 mol diamine (1,2-diaminoethane, 1,3-diaminopropane, 1,6-diaminohexane) and 0·025 mol PTCDA was suspended in 120 ml toluene and refluxed for 3 h. After cooling to room temperature, 200 ml 5% KOH solution was added and the mixture then stirred for 12–15 h to remove unreacted PTCDA. The crude diimides were separated by centrifugation. The residue was washed with water until the washings did not show any green fluorescence. The product was dried at 80–100°C. In order to remove polymeric diimides, compounds **2g** were dissolved in formic acid, stirred for 3 h and left overnight. The suspension was then filtered using cotton wool to remove the insoluble oligomer by-products; the diimide was finally precipitated by dropwise addition to 700 ml ethanol.

MS: **2g** (n = 6) (DCI^+ [NH_3]): *m/z* (%) = 589 (95), 574 (65), 475 (15), 517 (35), 490 (60), 475 (15). **2g** (n = 6) (DCI^- [NH_3]): *m/z* (%) = 588 (100).

UV/vis: **2g** (n = 2, 3, 6) [H_2O, 0·06 M NaOH, 0·05 M SDS]: λ (log ε) = 462 ± 1 (4·16–4·19), 490 ± 1 (4·58–4·6), 529 ± 1 (4·77–4·79) nm. **2g** (n = 2) [HCOOH]: λ = 462, 493, 530 nm. **2g** (n = 3) [HCOOH]: λ = 463, 494, 531 nm.

Fluorescence: **2g** (n = 2, 3, 6) [H_2O, 0·06 M NaOH, 0·05 M SDS]: λ = 540 ± 3 nm.

IR: **2g** (n = 2) [KBr]: ν = 3370 (m), 2943 (m), 1690 (vs), 1652 (vs), 1595 (vs), 1580 (sh), 1440 (w), 1405 (w), 1365 (w), 1340 (s), 1260 (m), 1160 (w), 1107 (w), 864 (w), 810 (m), 802 (w), 730 (m), 630 (w) cm^{-1}. **2g** (n = 3) [KBr]: ν = 3370 (m), 2943 (m), 1690 (vs), 1652 (vs), 1595 (vs), 1580 (sh), 1440 (w), 1405 (w), 1365 (w), 1340 (s), 1260 (m), 1160 (w), 1107 (w), 864 (w), 810 (m), 802 (w), 730 (m), 630 (w) cm^{-1}. **2g** (n = 6) [KBr]: ν = 3370 (m), 2943 (s), 1690 (vs), 1650 (vs), 1595 (vs), 1580 (sh), 1440 (m), 1405 (m), 1266 (w), 1340 (s), 1260 (m), 1160 (w), 1107 (w), 863 (w), 810 (m), 802 (w), 730 (m), 630 (w) cm^{-1}.

^1H NMR: **2g** (n = 6) [CF_3COOD]: δ = 1·7 (m, 16 H, —$CH_2C_4\underline{H}_8CH_2ND_2$): 4·3 (m, 4H, $C\underline{H}_2C_4H_8CH_2ND_2$); 4·9 (m, 4H, —$CH_2C_4H_8C\underline{H}_2ND_2$); 8·5 (m, 8H, $H_{arom.}$) ppm.

Elemental analysis: **2g** (n = 2) $C_{28}H_{20}N_4O_4$ (476·0) found: C 69·8 H 4·33 N 9·09; calculated: C 70·6 H 4·2 N 9·18. **2g** (n = 3) $C_{30}H_{24}N_4O_4$ (504·0) found: C 69·45 H 4·28 N 10·28; calculated: C 71·4 H 4·8 N 11·1.

2g (n = 6) $C_{36}H_{36}N_4O_2$ (556·0) found: C 72·48 H 5·74 N 7·25; calculated: C 73·5 H 6·1 N 9·5.

*4.2.3 General procedure for **Method III**: synthesis of 3,4,9,10-perylene-bis-(N,N'-[2-carboxyethyl]-carboximide) **2h** (n = 1), 3,4,9,10-perylene-bis-(N,N'-[3-carboxypropyl]-carboximide) **2h** (n = 2), 3,4,9,10-perylene-bis-(N,N'-[5-carboxypentyl]-carboximide) **2h** (n = 4), 3,4,9,10-perylene-bis-(N,N'-[6-carboxyhexyl]-carboximide) **2h** (n = 5)*

The dipotassium salts of **2k** were prepared in the following manner. PTCDA (1·31 mmol) was suspended in 50 ml DMSO, and the suspension was heated to 100°C with stirring. A solution of 31·8 mmol of the appropriate amino acid (amino-acetic, 3-amino-propionic, 5-amino-valerianic, 6-amino-capronic acid) and 31·8 mmol KOH in 25 ml water was added dropwise to the suspension, and the mixture was then stirred at 100°C for 3 h. The resultant suspension was cooled to room temperature and the precipitate collected, washed three times with 67 vol% DMSO/33 vol% H_2O and three times with methanol or a methanol–ethanol mixture, and dried. The yield of the dipotassium salt was 100% based on PTCDA. The salt was stored in a desiccator due to its slightly hygroscopic character.

The diacid forms of the dyes were obtained by suspending the dipotassium salt in hot aqueous 0·5 M HCl solution and stirring for 5 min. The resultant solid was washed three times with water and dried.

UV/vis: **2h** (n = 1,2,4,5) [H_2O, 0·06 M NaOH, 0·05 M CTAC]: λ (log ε) = 460 ± 1 (3·19–4·22), 490 ± 1 (4·58–4·60), 529 ± 1 (4·79–4·80) nm.

Fluorescence: **2h** (n = 1,2,4,5) [H_2O, 0·06 M NaOH, 0·05 M CTAC]: λ = 540 ± 3 nm.

IR: **2h** (n = 1) [KBr]: ν = 3500 (m-s, broad), 3050 (sh), 2937 (sh), 2856 (vw), 1687 (vs), 1658 (s), 1650 (s), 1630 (sh), 1592 (vs), 1577 (sh), 1439 (m), 1402 (m), 1369 (s), 1344 (m), 1300 (m), 1255 (m), 1174 (m), 1006 (m), 863 (w), 811 (m), 757 (s), 636 (m) cm^{-1}. **2h** (n = 2) [KBr]: ν = 3500 (m-s, broad), 3060 (sh), 2856 (w), 2740 (vw), 1695 (s), 1658 (vs), 1645 (sh), 1630 (w), 1592 (s), 1573 (s), 1557 (sh), 1403 (m), 1370 (s), 1341 (s), 1270 (w), 1255 (w), 1174 (w), 1126 (w), 1066 (w), 854 (vw), 810 (w), 749 (w), 615 (w) cm^{-1}. **2h** (n = 4) [KBr]: ν = 3500 (m-s, broad), 3060 (sh), 2956 (m-w), 2856 (w), 1692 (s), 1658 (vs), 1650 (sh), 1645 (sh), 1633 (w), 1614 (sh), 1592 (vs), 1574 (s), 1566 (s), 1563 (s), 1556 (s), 1537 (w), 1503 (w), 1442 (m), 1403 (m), 1349 (m), 1344 (m), 1250 (m), 1126 (m), 1066 (w), 853 (w), 809 (m), 746 (m), 618 (m) cm^{-1}. **2h** (n = 5) [KBr]: ν = 3500 (m-s, broad), 2935 (m), 2853 (m), 1693 (s), 1682 (m), 1657 (vs), 1650 (vs), 1644 (sh), 1633 (m), 1591 (s), 1573 (m), 1567 (m), 1555 (m), 1551 (m), 1441 (w), 1401 (m), 1343 (m), 1249 (w), 1160 (w), 1112 (w), 1079 (w), 852 (w), 809 (m), 746 (m), 636 (w) cm^{-1}.

Elemental analysis: **2h** (n = 1) $C_{28}H_{12}N_2O_8K_2$ (582·0) found: C 57·14 H

2·32 N 4·8; calculated: C 57·7 H 2·06 N 4·81. **2h** (n = 2) $C_{30}H_{16}N_2O_8K_2$ (610·0) found: C 58·59 H 2·67 N 4·62 O 20·84; calculated: C 59 H 2·6 N 4·6 O 21. **2h** (n = 5) $C_{36}H_{28}N_2O_8K_2$ (694·0) found: C 61·63 H 4·33 N 4·03; calculated: C 62·2 H 4·03 B 4·03.

4.2.4 *General procedure for the preparation of* ***3a-l*** *by alkylation of* ***2b-d***

Mixtures of 0·01 mol sublimed PTCDIs **2b-d** and a tenfold excess of the appropriate alkyliodide ($C_nH_{2n+1}I$; n = 1, 6, 12, 16) were suspended in 30 ml distilled DMF and refluxed for 18 h. After cooling the mixtures to room temperature, 50 ml methanol was added, and the mixtures stirred for 30 min. The crude products were separated by centrifuging. The precipitates were suspended in acetone, refluxed for 60 min and centrifuged. This procedure was repeated three times. The diimides were finally treated with petroleum ether (bp. 50–70°C) under reflux for 60 min. The products were separated using a centrifuge and dried at 90°C in vacuum. Yields between 85 and 97% were obtained.

UV/vis: **3a,b** [H_2O, 0·06 M NaOH, 0·05 M SDS]: λ (log ε) = 462 ± 1 (4·16–4·19), 491 ± 1 (4·59–4·61), 528 ± 1 (4·78–4·79) nm.

Fluorescence: **3a,b** [H_2O, 0·06 M NaOH, 0·05 M SDS]: λ = 539 ± 3 nm. **3a-l** [DMSO]: λ = 539 ± 3 nm.

IR: **3a-d** [KBr]: ν = 3500 (m, broad), 3017 (vw), 2959 (vw), 1696 (vs), 1650 (vs), 1592 (vs), 1573 (m), 1557 (sh), 1504 (vw), 1465 (w), 1439 (m), 1403 (m), 1370 (vw), 1345 (sh), 1270 (s), 1262 (m), 1187 (w), 1067 (w), 980 (w), 850 (w), 810 (m), 747 (m), 612 (vw) cm^{-1}. **3e-h** [KBr]: ν = 2920 (s), 2849 (m), 1708 (s), 1663 (s), 1591 (m), 1359 (m), 1253 (m), 809 (w), 791 (w), 744 (w), 630 (w) cm^{-1}. **3i-l** [KBr]: ν = 3500 (w, broad), 3048 (w), 3018 (w), 2960 (w), 2910 (w), 1698 (vs), 1658 (s), 1590 (s), 1573 (m), 1504 (w), 1439 (w), 1403 (m), 1370 (sh), 1345 (s), 1262 (m), 1168 (w), 1128 (w), 1024 (m), 850 (w), 810 (m), 747 (w), 612 (w) cm^{-1}.

Elemental analysis: **3a** $C_{36}H_{38}N_4O_4I_2$ (848·0) found: C 50·66 H 4·38 N 6·34; calculated: C 51·2 H 4·54 N 6·63. **3e** $C_{52}H_{30}N_4O_4I_2$ (1028·64) found: C 60·21 H 2·36 N 5·12; calculated: C 60·72 H 2·94 N 5·45. **3i** $C_{36}H_{16}N_4O_4I_2$ (822·36) found: C 50·96 H 1·88 N 6·20; calculated: C 52·58 H 1·96 N 6·81.

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