Research article

Binary Fluorescence Labeling for the Recovery of Polymeric Materials for Recycling

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Abstract

Fluorescent perylene derivatives for the invisible digital coding of polymers were reported where a binary combination of fluorescent doping allows the unambiguous identification of the polymers for sorting. The mono-material recovery of the polymeric materials is an important prerequisite for the high-performance application of recycled material and was enabled by the application of optical methods. **Copyright © IJESTR, all rights reserved.**

Keywords: Recycling, Labeling, Recovery, Fluorescence, Coding

Introduction

The recycling of organic macromolecular materials is an important problem both for economy and the protection of the environment. A circulation of matter is to be targeted for synthetic polymers as it is already reality for noble metals. Thermoplastic materials are of special interest for efficient recycling because of simple processing by melting and remolding. However, the common immiscibility of polymers is the main obstacle for such a technology because the performance of the recycled material decreases rapidly with the increasing content of polymeric contaminant. More than 5 % contaminant is not tolerable because of limitations of application; a purity of more than 99 % is targeted for high-performance applications. As a consequence, an efficient sorting of the material is a

prerequisite for such applications. Physical methods are described [1] for the detection and sorting of polymers such as using the density or electrostatic properties; on the other hand, a labeling of the polymers and the detection of the labeled material is attractive because a maximum of reliability can be expected.

A labeling of polymers for secure recognition for recycling is preferentially introduced for optical methods because of far developed and efficient technology. A simple coloration is less useful for labeling because of interference with other coloration. A fluorescence labeling [2] would be an attractive alternative where the concentration of doping material for labeling should be so low that no coloration is visually detected. A variety of fluorescence labels may be applied where we prefer purely organic fluorescent dyes because of degradability. Inorganic fluorophores for labeling such as rare earth elements-containing ceramics proved to be persistent and thus, would even increase the persistent man-made waste.

Materials and Method

Spectroscopy: UV/Vis absorption spectra: Varian Cary 4000; fluorescence spectra: Varian Eclipse; IR spectra: Perkin Elmer BX II FT-IR with an ATR unit; NMR spectra: Bruker, AMX 600; mass spectra: Finnigan MAT 95Q, JEOL JMS-700, Bruker Daltonics autoflex II.

Materials: The fluorescence labels **2** (TAS061) [3],**3** (S-13) [4], **4** TAS063) [5], **5** (TAS063.2) [5], **7** (AH-57) [6], and **8** (AH-151) [7] were prepared according to the literature. Technical POM pellets (polyoxymethylene) from DuPont were applied and melt and co-extruded with the fluorescent labels. Spectroscopic grade solvents were applied.

Imidazoloterrylene 6 (AH-198): Terrylene-3,4:11,12-tetracarboxylic-3,4:11,12-bis(1-hexylheptylimid)e [6] (**7**, 100 mg, 0.114 mmol) and freshly pulverized sodium amide (99 %. in crystalline platelets, 86.0 mg, 2.20 mmol) were dispersed in benzonitrile (11 mL), heated at 165 °C for 3 h, allowed to cool, shaken with a mixture of 2 N aqueous HCl and chloroform (1:1, 15 mL), collected with the organic phase, dried with magnesium sulphate, evaporated until dry (15 mBar and then medium vacuum to remove the excess of benzonitrile), dissolved in chloroform, filtrated and purified by column separation (silica gel, chloroform/*iso*-Hexane 3:1). Yield 78 mg (69 %) green solid, m.p. >250 °C. R_f (silica gel, chloroform) = 0.89. IR (ATR): $\tilde{\nu}$ = 3409.5 (w), 2951.5 (w), 2919.5 (m), 2851.9 (m), 1680.6 (m), 1652.6 (m), 1636.3 (s), 1617.0 (s), 1576.3 (s), 1531.8 (m), 1516.2 (w), 1483.8 (m), 1462.7 (m), 1452.7 (m), 1419.9 (m), 1384.1 (w), 1336.8 (vs), 1311.3 (s), 1296.7 (s), 1252.5 (m), 1206.3 (m), 1168.1 (m), 1052.6 (m), 1023.6 (m), 952.8 (m), 911.6 (m), 875.0 (m), 838.7 (m), 806.0 (s), 774.3 (m), 764.9(m) 750.2 (m), 722.6 (m), 694.6 (m), 682.0 (s), 657.6 cm^{-1} (m). ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 0.88–0.99 (m, 12 H, CH$_3$), 1.30–1.55 (m, 32 H, CH$_2$), 1.95–2.13 (m, 4 H, β-CH$_2$), 2.25–2.41 (m, 4 H, β-CH$_2$), 5.15–5.32 (m, 2 H, NCH), 6.96–7.21 (m, 3 H, CH$_{aryl}$), 7.30–7.40 (m, 2 H, CH$_{aryl}$), 7.51–8.747 (m, 9 H, CH$_{perylene}$), 9.71-9.87 (m, 1 H, CH$_{perylene}$), 10.42 ppm (s, 1 H, NH). ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C): δ = 14.2, 22.7, 27.2, 27.4, 29.4, 29.5, 29.7, 31.9, 32.5, 54.4, 118.5, 120.4, 120.8, 121.8, 122.3, 126.1, 128.3, 129.2, 129.9, 134.8, 141.3, 154.1, 163.6 ppm. UV/Vis (CHCl$_3$): λ_{max} (□) = 258.6 (50700), 320.8 (11700), 444.8 (6720), 481.6 (3960), 595.8 (11500), 645.8 (37970), 709.0 nm (82600). Fluoreszenz (CHCl$_3$, $\lambda_{excit.}$ = 525.0 nm): λ_{max} (I_{rel}) = 725.1 (1.00), 800.0 nm (0.40). Fluorescence quantum yield (CHCl$_3$, □$_{exc}$ = 645.2 nm, $E_{645.0\ nm/1\ cm}$ = 0.0101, reference S-13 (**3**) with □□□□1.00): >0.17. MS (DEI$^+$/70 eV): m/z (%): 995.5 [M^+ + H] (42), 995.5 [M^+] (16), 746.2 (12), 631.1 (20), 630.1 (33), 182.2 (29), 111.1 (13), 98.1 (16), 97.1 (36), 91.1 (20), 84.1 (29), 83.1 (53), 71.1 (17), 70.1 (56), 69.1 (94), 68.1 (12), 67.1 (21), 57.1 (43), 56.1 (61), 55.1 (100), 54.1 (25), 53.1 (11), 42.9 (51), 41.9 (24), 40.8 (58). HRMS (C$_{67}$H$_{70}$N$_4$O$_4$): Calcd. 994.5397, found 994.5387, Δ = − 0.0010. C$_{67}$H$_{70}$N$_4$O$_4$ (994.5): Calcd. C 80.85, H 7.09, N 5.63; found C 79.97, H 6.87, N 5.84.

Results and Discussion

The labeling of polymers in the optical spectral region is limited to a window of about 400 until about 1500 nm. The UV-light absorption of technical polymers below 400 nm interferes with the optical excitation of the fluorescence label and sets the hypsochromic limit of the applicable spectral window. On the other hand, light detection becomes more and more difficult with increasing wavelengths in the near infrared and thus, sets the bathochromic limit. An individual labeling of each type of polymer with a fluorophor emitting in a certain region of wavelengths would limit the method to a comparably small number of realizations because of the comparably high bandwidth of the fluorescence spectra of organic fluorophores; the independent detection of about maximal 12 individual labels seems to be realistic. A much higher manifold of possibilities is given by a binary combination of labels so that either the first one or the second or both chromophores are present and so on. As a consequence, 2^{n-1} realizations result for n chromophores (the lack of label has to be reserved for the detection of external material).
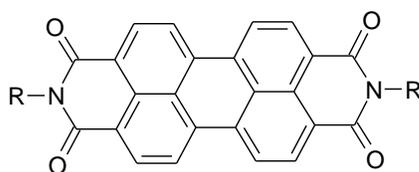

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The selection of fluorescent doping dyes means a compromise between long-term stability and degradability. Organic fluorescent dyes consisting of first and second period elements are attractive for such purposes because of unproblematic degradability; the *peri*-arylenes [8] such as the perylene dyes **1** [9] certify by their high fluorescent quantum yields and light-fastness being a good prerequisite for labeling applications. An alteration of the aromatic core and the carboxylic imide structures controls the position of the absorption and fluorescence maxima and allows an adaption to the special requirements for labeling. The hypsochromic visible region between 400 and 430 nm proved to be less suitable for the fluorescence of labels because of interference by genuine fluorescence of technical polymeric materials.
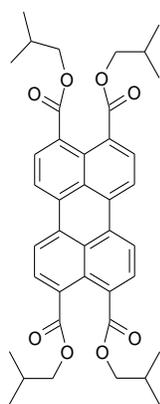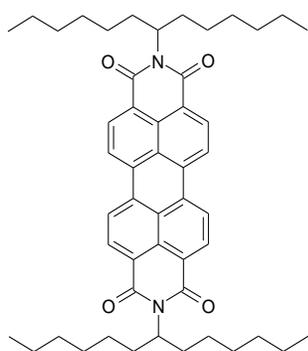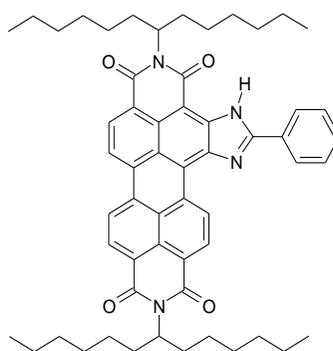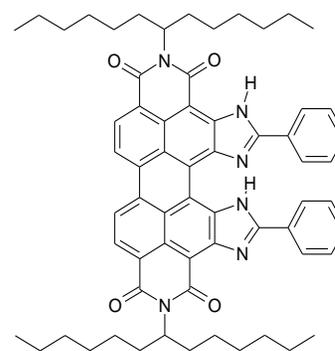
2   **3**   **4**   **5**

As a consequence, we applied the perylene ester **2** with a fluorescence maximum at 490 nm as the most hypsochromic label. The homologue tetramethyl-ester of perylene tetracarboxylic acid was reported as a fluorescence standard with a fluorescence quantum yield of close to unity [10]. However, the solubility is limited in

polymeric materials so that we applied the better soluble more branched tetra-isobutyl ester **2** as an alternative. The absence of stereogenic centers in the isobutyl group is important because otherwise difficult separable mixtures of diastereomers would be formed. The perylene-3,4:9,10-tetracarboxylic bisimides with fluorescence maxima at 535 nm cover the next spectral region. The *sec*-alkyl groups (swallow-tail substituents) in **3** are important for solubilizing. A bathochromic spectral shift of the basic chromophore can be introduced by the lateral condensation of heterocyclic groups; the imidazolo structure in **4** shifts the fluorescence to 598 nm, where a shift to 671 nm is obtained with the second heterocyclic ring in **5**. An axial extension of **4** means the terrylene derivative **6** with an even more bathochromic fluorescence at 727 nm. Figure 1 gives an impression of spectral region of the absorption and fluorescence of the labels.

6   **7**   **8**
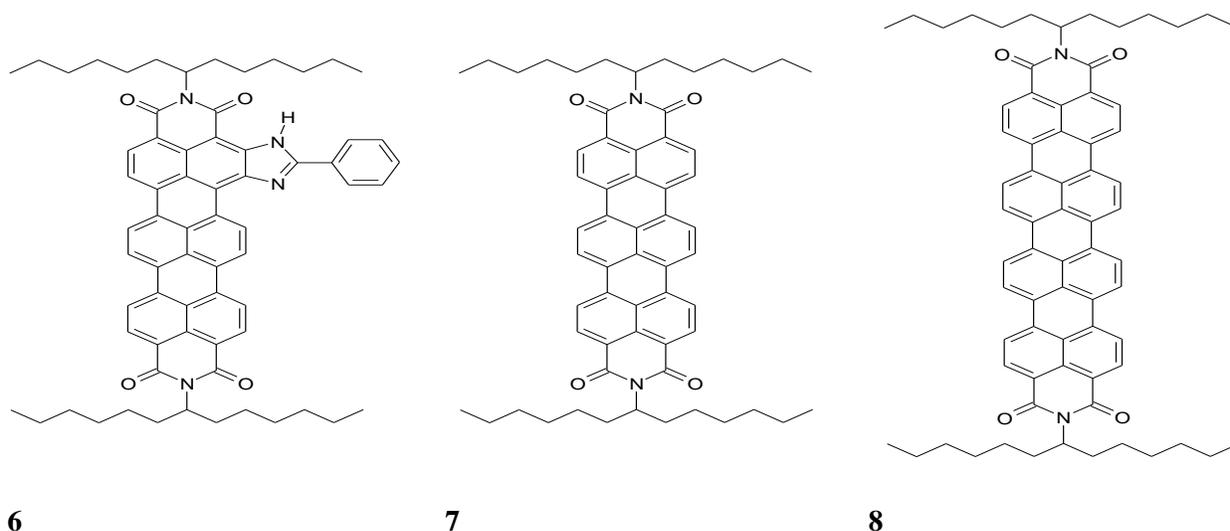
The label **4** may be replaced by the terrylene derivative **7** with a similar fluorescence spectrum and quantum yield nearby unity; a novel synthetic procedure [6] makes the biscaboximide **7** easily accessible. The number of labels can be further extended using the next bathochromic spectral region. For example, by the application of the quaterrylene derivative **8** where the absorption is as bathochromic as 761 nm and the strong fluorescence extends far into the NIR; on the other hand, the detection of such bathochromic light becomes more and more difficult. As a consequence, an extension of the fluorescence is recommended to long wavelengths until the fluorescence of **5** for routine applications and the further bathochromic region may be used for special requirements.

The fluorescence spectrum for the most unfavorable case of coding is reported in Figure 2 where all four fluorescent substances are added and are all fluorescent; this corresponds to a logical 1111. The individual fluorescence spectra of **2** … **5** are also shown in Figure 2 for comparison. There is some overlap of the fluorescent spectra because of vibronic structures, however, the maxima can be still unambiguously and clearly detected even in this worst case. An unambiguous detection was possible at a concentration below 0.1 ppm; an internal calibration with the Raman emission of matrix [11] may be helpful.

The detection of the labels can be further improved by the application of derivative spectra. The second derivative proved to give the most suitable results. However, the signal to noise ratio declines by the formation of each derivative becoming even more important for the second derivative. A moving average was formed in order to overcome this problem. The upper curve in Figure 2 was calculated as the sliding average of 50 measurements within 10 nm. The resulting sharpening of lines of the individual fluorescence by the second derivative simplifies

the application of a threshold so that a discrimination becomes more simple and efficient; see the upper dashed line in Figure 2.
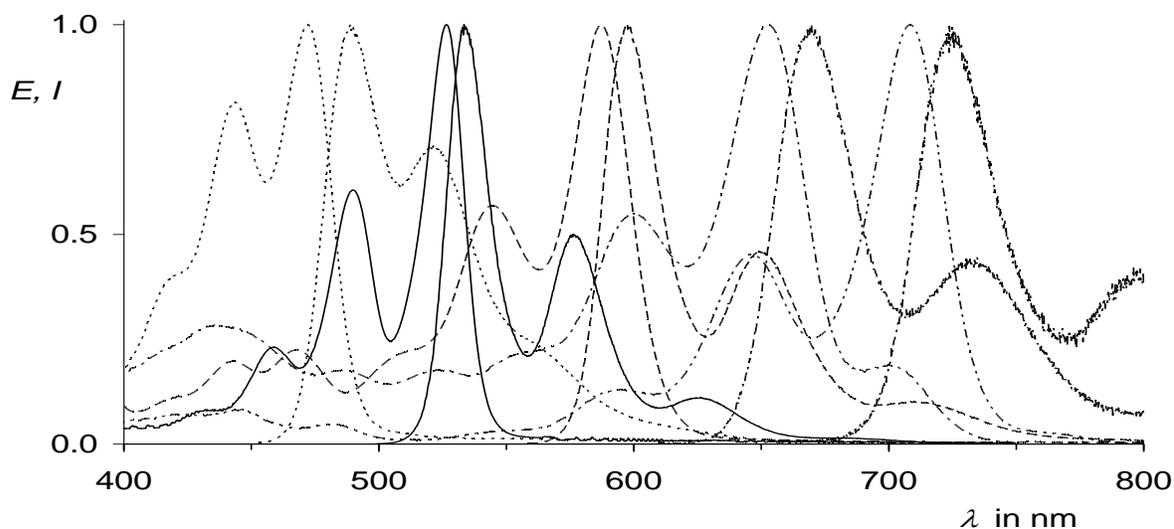

Figure 1: Absorption (left) and fluorescence (right) spectra of the fluorescence labels in chloroform of **2** (dotted), **3** (solid), **4** (dashed), **5** (dotted dashed), and **6** (double dotted dashed).
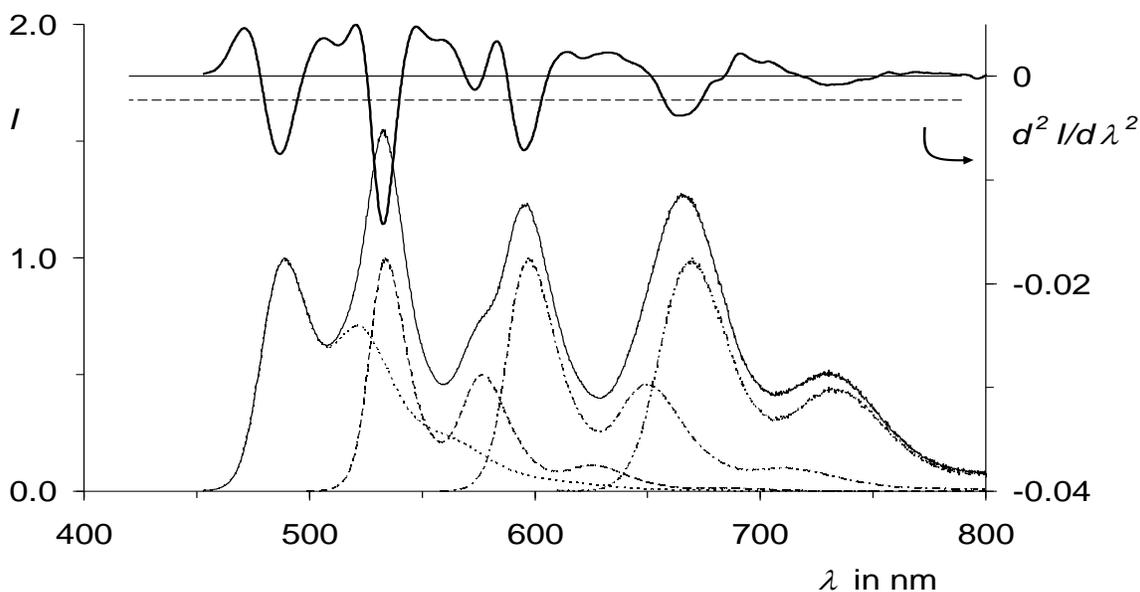

Figure 2: Fluorescence spectra of labels in chloroform (left scale). **2** (dotted), **3** (dashed), **4** (dotted dashed), and **5** (double dotted dashed). Solid line: added spectra. Right scale and upper solid line: Second deviation of the added spectra.

The formation of the fourth derivative would further sharpen the lines, however, the signal to noise ratio declines appreciably. As a consequence, the use of the second derivative seems to be the best compromise for practical application. The derivatives can be easily calculated by the consecutive formation of differences and a power of two is preferably applied for the sliding average for simplifying calculations. The application of integer arithmetic is fully sufficient for signal processing. Thus, the process of calculation becones essentially reduced to integer additions; comparably simple and efficiently operating electronic chips are therefore suitable and available.

One can further expand the combinations for detection by the application of an additional chromophore with a more bathochromic fluorescence outside the window for the detection of **2** ... **5**. ; the possibilities are restricted because both bathochromic fluorescence and high photostability are required. The terrylene derivative **6** proved to be suitable for such an application (absorption 707 nm, fluorescence 726 nm), However, the fluorescence at comparably long wavelengths increases the demands concerning the detector. This additional marker may be applied for the expansion of combinations to 31 materials. On the other hand, an application for the introduction of redundancy would increase the reliability of sorting the polymers or its application for internal calibration of fluorescence.
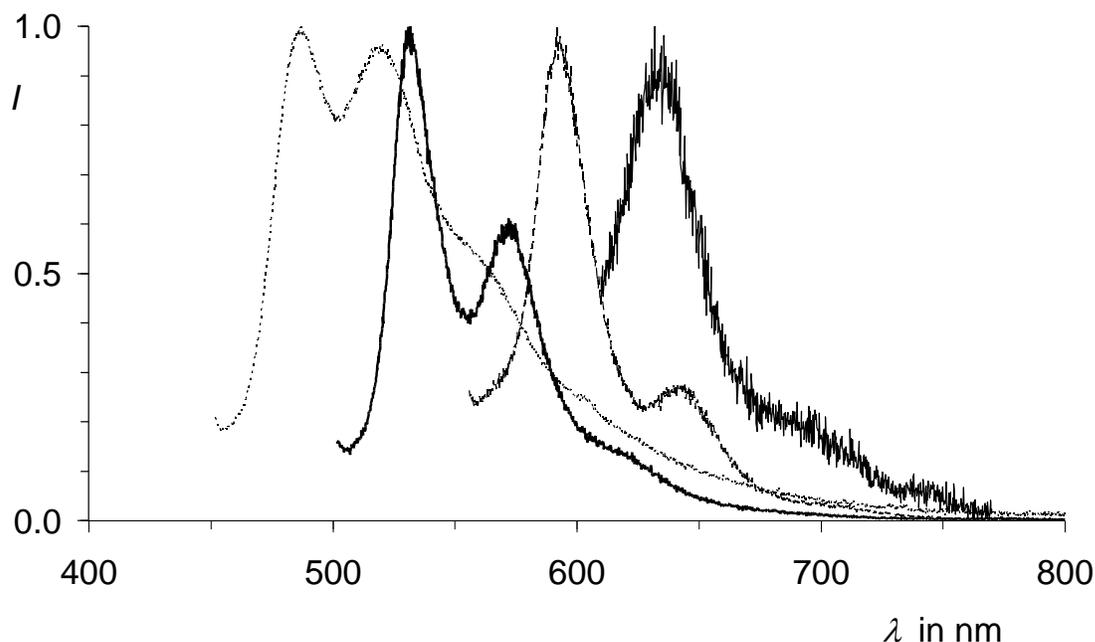

Figure 3: Labeling of polyoxomethylen (POM). Fluorescence of the dyes **2** ... **5** (from left to right).

Thus, the prerequisites for a practical application of the fluorescence labeling is given. Figure 3 indicates the labeling of polyoxymethylen (POM) with the dyes **2** ... **5** under unfavorable conditions. The spectra are similar to Figure 2; there is only a very weak medium effect on the fluorescence. The concentration of the applied labels is important and should be below 0.1 ppm in order to avoid re-absorption and visible coloration of the polymeric material. The influence of beginning re-Absorption can be seen in the spectrum of **2** where the first vibronic band is weakened; the detector may be adapted in such cases. Genuine, non-colored technical POM was used for the test in Figure 3. It may be necessary to increase the amount of doping material for strongly colored polymers such as

purely black polymers where a concentration of 20 ppm is still sufficient for detection. Standard mixing and extruding is appropriate for routine coloration of polymers whereas special care is necessary for polymeric materials darkly colored with carbon black. The latter may act such as charcoal and partially adsorb the dyes for labeling where we recommend the extruding of a small amount of the uncolored polymer with the whole amount of dyes for labeling and then a further co-extruding with all the polymer to be labeled. Alternatively, good results with black POM were obtained with a mixing at high temperature (more than 480 °C) and a short time for mixing with the dyes.
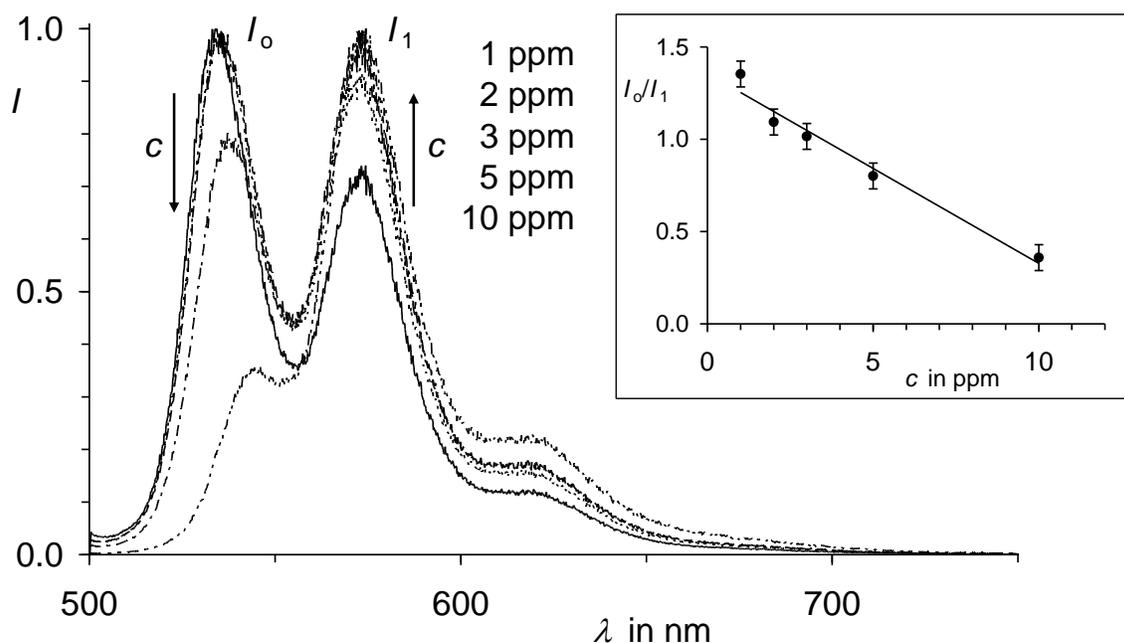

Figure 4: Fluorescence spectra of **2** in solid POM (polyoxymethylene) at various concentrations (1 ppm solid, 2 ppm dotted, 3 ppm dashed, 5 ppm dotted dashed, 10 ppm double dotted dashed line). Insert: Ratio of the second vibronic band (I_o) to the first one (I_1) as a function of the concentration c of **3** in ppm. $I_o/I_1 = -0.103 \cdot c/\text{ppm} + 1.36$; correlation number -0.98 for 5 points; standard deviation of the slope 0.01; standard deviation of the intercept 0.07.

The addition of higher concentrations of fluorescence labels changes the spectra by re-absorption of the fluorescent light; see Figure 4. On the other hand, this effect may be applied for further coding if a slight visible coloration of the polymer can be tolerated and dyes with pronounced vibronic structure in the fluorescence are applied such as **2** ... **7**. The ratio of the intensity of the most hypsochromic band (I_o) over the next vibronic band (I_1) is dependent on the concentration c of the applied dye and may be even linearized; see the insert in Figure 3. The discrimination of four different concentrations seems to be realistic. Thus, the combinations for labeling were amplified by a factor of 16 to obtain 240 possibilities.

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Conclusion

Perylene derivatives are principally suitable for binary coded fluorescence labeling of materials. This class of dyes is a good compromise between (1) sufficiently high photostability for long-lasting marking for recovery and (2) avoiding the introduction of additional persistent material where (3) the toxicity seems to be extraordinarily low [12]. Four dyes are presented with fluorescence in the visible enabling the coding of 15 materials. At higher concentrations of the labels alterations in the spectra by re-absorption of fluorescent light allows a further discrimination so that 240 different realizations become possible. An additional fluorescent dye with a more bathochromic fluorescence can be applied for the extension of coding, the increase of reliability by redundance, or internal calibration.

Acknowledgement

References

[1] (a) Nemeth, E., Schubert, G., Albrecht, V., Simon, F.; Aufbereitungs Tech. 46, 2005, 35-46. (b) Nemeth, E., Simon, F., Albrecht, V., Schubert, G.; Ger. Patent (2006), DE 102004024754 B3 (May 12. 2004); Chem. Abstr. 144, 2006, 392348. (d) Gohs, U., Albrecht, V., Husemann, K,. Reinsch, E., Schuenemann, R., Simon, F., Ger. Offen. (2009), DE 102007055765 A1 (Dec. 11, 2007); Chem. Abstr. 151, 2009, 57663.

[2] (a) Corbet, E. C. Frey, J. G., Groce, R. I., Hendra, P. J., an investigation into the applicability of luminescent tagging to polymer recovery, Plastics, Rubber and Composite Processing and Application 21, 1994, 5-11. (b) Rafi Ahmad, S., marking of products with fluorescence tracers in binary combinations for automatic identification and sorting, Assembly Automatation, 20, 2000, 58-65. (c) Alam, M. K. Stanton, S. L. Hebner, G. A., near infrard spectroscopy and neural network for resin identification, Spectroscopy 9, 1994, 31-39. (d) Scott, D. M., a two-colour near infra-red sensor for sorting recycled plastic waste, Meas. Sci. Tech. 6, 1995,156-159. (e) General Electric Company; Hubbad, S., Potyrallo, R., Schottland, P., Thomas, V.; tagging materials for polymers, methods, and articles made thereby; U.S. Patent 2005/0095715 (May 5, 2006).

[3] Alibert-Fouet, S., Seguy, I., Bobo, J.-F., Destruel, P., Bock, H.; liquid-crystalline and electron-deficient coronene oligocarboxylic esters and imides by twofold benzogenic diels-Alder reactions on perylenes , Chem. Europ. J. 13, 2007, 1746-1753.

[4] (a) Rademacher, A., Märkle, S., Langhals, H.; Loesliche Perylen-Fluoreszenzfarbstoffe mit hoher Photostabilitaet, Chem. Ber. 115, 1982, 2927-2934. (b) Langhals, H., Demmig, S., Potrawa, T.; the relation between packing effects and solid state fluorescence of dyes, J. Prakt. Chem. 333, 1991, 733-748.

[5] Langhals, H., Kinzel, S., Obermeier, A.; Imidazoloperylenbisimide, Ger. Offen. DE 102008061452.1 (December 10, 2008); Chem. Abstr. 151, 2009, 58174.

[6] (a) Langhals, H., Walter, A., Rosenbaum, E., Johansson, L. B.-Å.; a versatile standard for bathochromic fluorescence based on intramolecular FRET, Phys. Chem. Chem. Phys. 13, 2011, 11055-11059. (b) Langhals, H., Hofer, A.; synthesis and fluorescent properties of S-13-terrylene bisimides and terrylene-3,4: 11,12-tetracarboxylic acid bisanhydride, Ger. Offen. DE 102011018815.0 (April 4, 2011); Chem. Abstr., 2012, 157636339.

[7] (a) Langhals, H., Buettner, J., Blanke, P.; A two-step synthesis for quarterrylene bisimides. Application of the "green route" method, Synthesis 2005, 364-366. (b) Langhals, H., Schoenmann, G., Feiler, L.; a two-step synthesis of quaterrylenetetracarboxylic bisimides - novel NIR fluorescent dyes, Tetrahedron Lett. 36, 1995, 6423-6424.

[8] Review: Langhals, H., chromophores for picoscale optical computers, in Sattler, K. (ed.), fundamentals of picoscience, p. 705-727, Taylor & Francis Inc. CRC Press Inc., Bosa Roca/US 2013; ISBN 13: 9781466505094, ISBN 10: 1466505095.

[9] Reviews: (a) Langhals, H.; molecular devices. Chiral, bichromophoric silicones: Ordering principles in complex molecules, in Ganachaud, F., Boileau, S., Boury B. (eds.), silicon based polymers, p. 51-63, Springer, 2008, ISBN 978-1-4020-8527-7, e-ISBN 978-1-4020-8528-4. (b) Langhals, H., cyclic carboxylic imide structures as structure elements of high stability. Novel developments in perylene dye chemistry, Heterocycles 40, 1995, 477-500.

[10] Langhals, H., Karolin, J., Johansson, L. B.-Å.; spectroscopic properties of new and convenient standards for measuring fluorescence quantum yields, J. Chem. Soc., Faraday Trans. 94, 1998, 2919-2922.

[11] Aubert, C., Fuenfschilling, J., Zschokke-Graenacher, I., Langhals, 'H.; hochempfindliches Nachweisverfahren auf der Basis der Fluorescenz durch Laser-Anregung, Zeitschr. Analyt. Chem. 320, 1985, 361-364.

[12] Einsiedl, F., Wohnlich, S., Langhals, H., unpublished results.