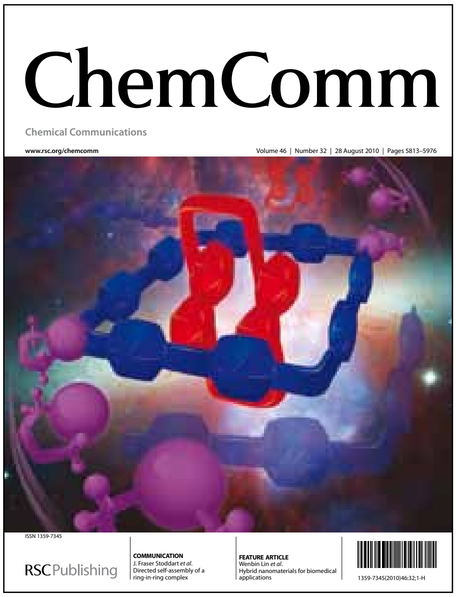
ChemComm

Accepted Manuscript



ChemComm

Chemical Communications

www.rsc.org/chemcomm

Volume 46 | Number 32 | 28 August 2010 | Pages 5813–5976

ISSN 1359-7345

RSC Publishing

COMMUNICATION
J. Fraser Stoddart *et al.*
Directed self-assembly of a ring-in-ring complex

FEATURE ARTICLE
Wenbin Lin *et al.*
Hybrid nanomaterials for biomedical applications

1359-7345(2010)46:32;1-H

This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSC Publishing

www.rsc.org/chemcomm

Registered Charity Number 207890

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Direct Detection of Ultralow Trace Amount of Isocyanates in Air Using Fluorescent Conjugated Polymer

Khama Rani Ghosh,[a] Sukanta Kumar Saha,[a] Jian Ping Gao,[a] Zhi Yuan Wang* [a,b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

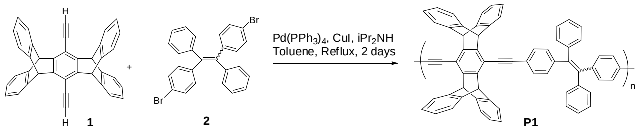
A fluorescence sensory polymer containing the pentiptycene and tetraphenylethylene units linked by acetylene was synthesized for direct detection of isocyanates in air. Eight industrially available aliphatic and aromatic isocyanates were tested. The polymer film shows a rapid fluorescence quenching response to any type of isocyanates with a ppt level of detection limit, which is much lower than the permissible exposure limit of 5 ppb.

Isocyanates are highly reactive and low molecular weight compounds containing the isocyanato group (-N=C=O). There are three common types of isocyanates available: mono-, di-/tri- and polyisocyanates and among them polyisocyanates are not volatile at room temperature.[1-4] Isocyanates readily react with compounds containing hydroxyl groups to produce urethanes or polyurethanes, which are widely used in the manufacture of flexible and rigid foams, fibers, coatings and elastomeric products. Isocyanates are widely used in large quantity in many industrial sectors, such as automobile, construction and sports. The most commonly used diisocyanates are 4,4-methylenedisocyanate (MDI), 2,4-toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 1,5-naphthalene diisocyanate (NDI), p-phenylene diisocyanate (PPDI).[5-8] Exposure to even a small amount of isocyanates can cause irritation of the eyes and skin and also decreased lung function when inhaled in the form of gas, stream, dust or aerosol.[9,10] The most common adverse health impact associated with isocyanate exposure is asthma due to sensitization. The long term and overexposure cause strong respiratory, cutaneous irritants, occupational asthma. On the other hand, rash, itching, hives, swelling of the extremities and hypersensitivity pneumonitis are caused by the less exposure to isocyanates.[11] In most countries, the permissible exposure limit (PEL) of most isocyanate monomers is 5 ppb in air.[12] This implies that the detection of isocyanate compounds in a workplace is highly required to maintain a safe working environment and protect the workers from adverse health effect. The most commonly used analytical methods for the detection of isocyanates in air are colorimetric methods,[13] absorption spectrophotometry,[14-17] liquid chromatography with fluorescence detection using N-methyl-1-naphthalenemethylamine as a fluorescence-activating reagent,[18] capilary zone electrophoresis as an alternative to HPLC,[19] and mass spectrometry.[20] A recently developed and improved method to detect isocyanates is PTR-MS (proton transfer reaction-mass spectrometry).[21] Nearly all the analytical techniques require chemical derivatizations and separation. Most methods are limited to a few isocyanates with the unknown detection limits, except for the one by alkaline adduct coordination ion spray tandem mass spectrometry for determining specifically three isocyanates (HDI, 2,4-TDI and 2,6-TDI) at ppt levels in air.[20a]

Highly fluorescent conjugated polymers are used as molecular sensors for direct detection of various chemicals, such as nitroaromatic explosives.[22,,23] Conjugated polymers are able to transfer their energy from the excited state to the electron deficient analytes and cause fluorescence turn-off. In comparison with nitro compounds, isocyanates are also electron deficient and have sufficient vapor pressure at room temperature. Accordingly, isocyanates should be detectable, like nitro compounds, by fluorescence quenching mechanism using a conjugated polymer.

For direct detection of isocyanates in air by fluorescence method, we designed a conjugated polymer containing the pentiptycene and tetraphenylethene (TPE) units that are linked by an acetylene bond, namely polymer **P1** (Scheme 1). Pentiptycene is selected as one of key structural components in polymer, since it is readily available by simple synthesis[24,25] and is proven to be useful in polymers for fluorescence detection of nitro explosives’[26] Pentiptycene has a three dimensional rigid structure, which prevents π-stacking or excimer formation in the excited state in the solid film.[26,27] TPE is a known luminophore and in particular is highly emissive in the aggregated state or has the aggregation-induced emission (AIE) efect.[28] In addition to some unique applications,[29-34] the polymers with the AIE property have been used as chemosensors.[35-37] Therefore, polymer **P1** is expected to be highly emissive as the solid film, due to the presence of the aggregated TPE moiety. The aggregated TPE and the bulky pentiptycene moieties create the molecular cavities in polymer film, which allow for the analytes entering and being trapped readily. Thus, these molecular features and characteristics are deemed to make polymer **P1** suitable for sensing various isocyanates.

Herein we represent the synthesis and properties of a sensory polymer with a high sensitivity towards isocyanates. Thin films of polymer **P1** is able to detect various aliphatic, aromatic, mono and diisocyanates at the permissible exposure limit at room temperature. In our work, we selected pentiptycene diacetylene (**1**) and 1,2-bis(4-bromophenyl)-1,2-diphenylethene (**2**) as monomers. Monomers **1** and **2** were synthesized according to the standard procedure from the literature.[38,39] The synthetic route to the target sensory polymer **P1** is shown in Scheme 1. The Sonogashira cross-coupling reaction of compound **1** with compound **2** affords polymer **P1** in 71% yield.



Scheme 1. Synthesis of polymer **P1** by Sonogashira cross-coupling reaction.

Polymer **P1** is highly soluble in THF and TCE and partially soluble in $CHCl_3$, CH_2Cl_2 and DMF. Polymer **P1** has an inherent viscosity of 0.20 dL/g in TCE at 30 °C and forms a uniform and smooth film on glass surface by casting or spin coating. The ^{1}H-NMR spectrum (Figure S1) of **P1** displays the peaks for aromatic protons at 6.2 to 7.2 ppm but no peak at 3.71 ppm for the acetylenic proton, indicating a reasonably high molecular weight. The band at 2203 cm^{-1} for the C≡C bond in the IR spectrum (Figure S2) also confirms the polymer formation. The further evidence comes from the 13C-NMR data (Figure S3), which clearly reveals that the acetylene carbons at 78.03 and 84.84 ppm for monomer **1** shift to 124.88 and 123.52 ppm for polymer **P1**. Figure S6 displays the normalized absorption and emission spectra of polymer **P1** in solution and in film. In solution, polymer **P1** has a maximal absorption at 363 nm whereas monomers **1** and **2** have the absorption maxima at 332 nm and 317 nm, respectively. Polymer **P1** emits at 488 nm, whereas the monomers **1** and **2** have the emission maxima at 356 nm and 437 nm, respectively. A red shift in absorption and emission spectra for polymer **P1** relative to monomers **1** and **2** is resulted from extension of π-conjugation in the polymer backbone. The film of polymer **P1** absorbs broadly in comparison with the one in solution and emits at 504 nm with a quantum yield of 17%. From SEM images (Figure S14C), the average pore size of the film surface is estimated to be 97 nm.

In sensing experiments, polymer films were exposed to the vapor of isocyanates at room temperature and the fluorescence spectra were recorded immediately after isocyanate exposure for a specific period. Fluorescence Quenching Response (FQR) can be defined as the percent ratio of fluorescence intensity decrease upon exposure and initial fluorescence intensity. Figure 1(a) displays the gradual changes of the fluorescence intensity upon exposure to MDI vapor over a period of 300 s. After 60 s of exposure to MDI, the fluorescence intensity of **P1** dropped by 74% or 74% FQR, and continued to drop by 84% at 300 s. Figure 1(b) shows the changes of the fluorescence intensity in the presence of IPDI vapor. The FQR was 52% at 60 s and 67% at 300 s. By comparing the FQR for MDI and IPDI, it can be concluded that polymer **P1** is sensitive towards both aromatic and aliphatic isocyanates.

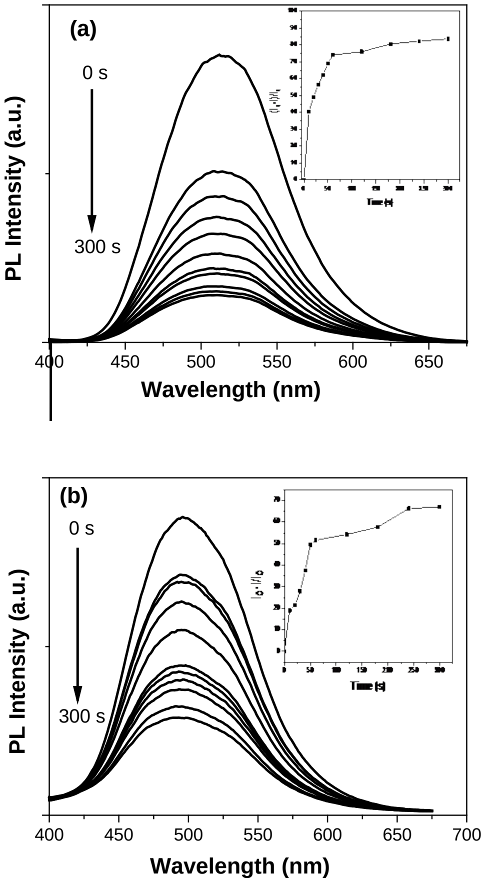


Figure 1. The time- dependent fluorescence intensity of **P1** film (7nm) upon exposure to (a) MDI (b) IPDI vapor (room temperature) from 0 s to 300 s.

In the isocyanato group, the carbon atom is partially positively charged, as it doubly bonded with more electronegative N and O atoms. These electronegative atoms are pulling electrons away from the carbon atom, making the isocyanato group quite electron deficient. The high reduction potential of isocyanato group allows for an easy electron transfer and thus effective fluorescence quenching. The pentiptycene and TPE moieties create a large number of cavities or free volume in polymer film, which permits a high diffusion rate for isocyanate molecules to enter the polymer film, thus leading to a high FQR within a short period of exposure. Experimentally, the fluorescence signals decrease noticeably within only 10 seconds of isocyanate exposure (Table 1) and become constant after 5 minutes, indicating that the concentration of analyte molecules in the polymer film with a thickness of 4-30 nm has reached the equilibrium at room temperature.

To further prove the sensitivity of polymer **P1** towards isocyanates, 8 different isocyanates, including phenyl isocyanate (PI), 4-methoxyphenyl isocyanate (MeOPI), 4-nitrophenyl isocyanate (NO_2PI), 4,4-methylene diisocyanate (MDI), 2,4-toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), p-phenylene diisocyanate (PPDI), were tested. The FQR data at given time are summarized in Table 1 and the other spectroscopic measurements are given in the supporting information.

Table 1. Fluorescence quenching response (%) at given time for various isocyanates using polymer **P1**[a].

Time, s	10	20	30	40	50	60	120	180	240
PPDI	23	31	48	54	63	71	75	78	81
MDI	41	49	56	62	69	74	76	81	82
TDI	22	30	42	52	60	63	67	70	75
PI	21	30	41	52	60	66	70	73	77
NO_2PI	14	18	32	40	49	61	66	69	72
MeOPI	22	31	41	45	54	59	61	65	66
HDI	24	26	40	45	53	62	67	71	73
IPDI	19	21	28	38	50	52	54	58	63

[a] The film thickness is in a range of 4-7 nm for all measurements.

At 60 s of exposure, the order of the FQR is MDI > PPDI > PI > TDI > HDI > NO_2PI > MeOPI > IPDI. The experimental results indicate that polymer **P1** can maintain a high sensitivity towards aliphatic and aromatic isocyanates. The detection sensitivity or FQR relates to the vapor pressure of the isocyanate. For aromatic mono-isocyanates, polymer **P1** shows a higher sensitivity towards phenyl isocyanate, due to the higher vapor pressure of PI (1.4 mmHg, Table S1) than that of MeOPI (0.107 mmHg) or NO_2PI (6.84×10^{-3} mmHg). The detection sensitivity is also related to the nature or reduction potential of isocyanates. Polymer **P1** shows a higher sensitivity towards aromatic diisocyanates than aliphatic diisocyanates, because the former is more electron deficient than the latter, even though MDI has a much lower vapor pressure (4.5×10^{-6} mmHg) than HDI (5.26×10^{-3} mmHg) or IPDI (3.0×10^{-4} mmHg). For the same reason, PPDI has a vapor pressure less than 6.0×10^{-3} mmHg but due to its highly electron-deficient nature causes the highest FQR for polymer **P1**. Since MDI has the lowest vapor pressure or vapor concentration of 0.062 ng/mL among all the eight isocyanates tested, the detection limit of polymer **P1** should be at a ppt level (i.e., 0.06 ppt) and is much lower than the permissible exposure limit (PEL) of 5 ppb.

The FQR value is higher for MeOPI than NO_2PI during the initial 60 s exposure but is lower for MeOPI than NO_2PI after 60 s. This time-dependent FQR is likely due to the different permeability of these two isocyanates in the polymer film. Since the gas permeation consists of adsorption of the permeating species into the polymer, diffusion through the polymer and desorption of the permeating species from the polymer surface and removal, the permeability can be affected by solubility and diffusivity of isocyanate molecules in the polymer film. At the beginning, the FQR is mainly controlled by the diffusion rate, which is governed by the vapor pressure. Therefore, MeOPI with a higher vapor pressure (0.107 mmHg) gives a higher FQR than NO_2PI (6.84×10^{-3} mmHg). At a later stage, the adsorption and desorption of isocyanate molecules in polymer reach an equilibrium and the FQR should now be governed by the isocyanate solubility in polymer. Thus, NO_2PI with a higher affinity gives a larger FQR than MeOPI.

In summary, a conjugated fluorescent polymer has been successfully synthesized and used for direct detection of various isocyanates in air. Polymer **P1** is highly sensitive to aromatic and aliphatic isocyanates with a detection limit at the ppt level. The isocyanate sensing under ambient conditions is fast, typically within a period of 10-60 s. A highly sensitive optical sensor based on **P1** or other similar conjugated polymers is feasible and applicable for direct monitoring the isocyanate chemicals at a workplace.

Notes and references

[a] *Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6*
[b] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China; E-mail: wayne_wang@carleton.ca*

† Electronic Supplementary Information (ESI) available: [^{1}H NMR, ^{13}C NMR and IR spectra of **P1**; absorption and fluorescence spectra of **P1** in solution and as film; vapor concentrations of each isocyanate; experiment details for fluorescence titration experiments of **P1**; SEM images of **P1** film]. See DOI: 10.1039/b000000x/

‡ This work was supported by the Natural Science and Engineering Research Council of Canada and National Natural Science Foundation of China (21134005, 21074132, 20920102032 and 20834001).

1 J. H. Saunders and R. J. Slocombe, *Chem. Rev*., 1948, **43**, 203.
2 R. G. Arnold, J. A. Nelson and J. J. Verbanc, *J. Chem. Edu*., 1957, **34**, 158.
3 M. Sato, *J. Am. Chem. Soc*., 1960, **82**, 3893.
4 M. Kaplan, *J. Chem. Eng*., 1961, **6**, 272.
5 R. B. Seymour and G. B. Kauffman, *J. Chem. Ed.*, 1992, **69**, 909.
6 Flexible polyurethane foams. Technical bulletin 2008, Doc. No. AX-239.
7 R. P. Streicher, C.M. Reh, R. Key-Schwartz, P. C. Schlecht and M. E. Cassinelli, *NOISH Manual of Analytical Methods* 2004, 116.
8 A Summary of Health Hazard Evaluations: *Issues Related to Occupational Exposure to Isocyanates, 1989 to 2002*, 2004,116.
9 L. H. Kormos, R. L. Sandridge and J Keller, *Anal. Chem.*, 1981, **53**, 1122.
10 L. T. Budnik, D. Nowak, R. Merget, C. Lemiere and X. Baur, *J. Occup. Med. Toxicol*., 2011, **6**, 9.
11 M. M. Methner, C. Achutan and A. Adebayo, *Health Hazard Evaluation Report*, 2004-0349-2970 and the references there in.
12 (a) Québec, éditeur officiel, Réglementation sur la santé et sécurité autravail, décret 885-2001, Québec, 2001, Canada. (b) American Conference of Governmental Industrial Hygienists, Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, Cincinnati, OH, 2004. (c) National Institute for Occupational Safety and Health Alert, Publication no. 1996-111, Cincinnati, OH, 1996. (d) Swedish National Board of Occupational Safety and Health, Occupational exposure limit values. Arbetarskyddsstyrelsens fösfattningssamling, AFS 2000: 3, Liber, Stockholm, Sweden, 2000. (e) Code of Federal Regulation (CFR), Government Printing Office, office of the federal register, 29 CFR *1910.1000, Washington DC, 1992.
13 (a) C. J. Purnell and R. F. Walker, *Analyst*, 1985, **110**, 893; (b) R. J. Rando and Y. Y. Hammad, *Am. Ind. Hyg. Assoc. J.*, 1985, **46**, 206.
14 (a) K. Marcali, *Anal. Chem*., 1957, **29**, 552; (b) K. E. Grim and A. L. Linch, *Am. Ind. Hyg. Assoc. J.,* 1964, **25**, 285.
15 J. Keller, K. L Dunlap and R. L. Sandridge, *Anal. Chem*., 1974, **46**, 1845.
16 J. Keller and R. L. Sandridge, *Anal. Chem.,* 1979, **51**, 1868.

17 R. F. Walker and M. A. Pinches, *Analyst*, 1979, **104**, 928.

18 L. H. Kormos, R. L. Sandridge and J Keller, *Anal. Chem*., 1981, **53**, 1122.

19 W, E. Rudzinski, L. Pin, R. Sutcliffe, A. Richardson and T. Thomas, *Anal. Chem*., 1994, **66**, *1664*.

20 (a) S. Gagné, J. Lesage, C. Ostiguy, Y. Cloutier and H. V. Tra, *J. Environ. Monit*., 2005, **7**, 145. (b) D. Karlsson, M. Spanne, M. Dalene and G. Skarping, *Analyst*, 1998, **123**, *117*.

21 B. Agarwal, S. Jürschik, P. Sulzer, F. Petersson, S. Jaksch, A. Jordan and T. D. Märk, *Rapid Commun., Mass Spectrom.* 2012, **26**, 983.

22 S.W. Thomas, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339.

23 X. Duan, L. Liu, F. Feng and S. Wang, *Acc. Chem. Res.*, 2009, **43**, 260.

24 E. Clar, *Chem. Ber*., 1931, **64**, 1676.

25 W. Theilacker, U. Berger-Brose and K.-H. Beyer, *Chem. Ber.*, 1960, **93**, 1658.

26 J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc*., 1998, **120**, 11864.

27 J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc*., 1998, **120**, 5321.

28 (a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun*., 2001, 1740; (b) B. Z. Tang, X. Zhan, G. Yu, P. P. S. Lee, Y. Liu and D. Zhu, *J. Mater. Chem*., 2001, **11**, 2974.

29 B. Xu, Z. Chi, H. Li, X. Zhang, X. Li, S. Liu, Y. Zhang and J. Xu, *J. Phys. Chem. C*, 2011, **115**, 17574.

30 X. Fan, J. Sun, F. Wang, Z. Chu, P. Wang, Y. Dong, R. Hu, B. Z. Tang and D. Zou, *Chem. Commun.*, 2008, 2989.

31 W.-E. Lee, C.-L. Lee, T. Sakaguchi, M. Fujikid and G. Kwak, *Chem. Commun*., 2011, **47**, 3526.

32 X. Zhou, H.-Y. Li, Z.-G. Chi, B.-J. Xu, X.-Q. Zhang, Y. Zhang, S.-W. Liu and J.-R. Xu, *J. Fluoresc.*, 2012, **2**, 565.

33 J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. Zhu and B. Z. Tang, *Chem. Mater*., 2003, **15**, 1535.

34 H. Li, X. Zhang, Z. Chi, B. Xu, W. Zhou, S. Liu, Y. Zhang and J. Xu, *Org. Lett*., 2011, **13**, 556.

35 W. Wu, S. Ye, L. Huang, L. Xiao, Y. Fu, Q. Qi Huang, G. Yu, Y. Liu, J. Qin, Q. Lia and Z. Li, *J. Mater. Chem*., 2012, **22**, 6374.

36 R. Hu, J. L. Maldonado, M. Rodriguez, C. Deng, C. K. W. Jim, J. W. Y. Lam, M. M. F. Yuen, G. Ramos-Ortiz and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 232.

37 Y. Liu, C. Deng, L. Tang, A. Qin, R. Hu, J. Z. Sun and B. Z. Tang, *J. Am. Chem. Soc*., 2011, **133**, 660.

38 T. Yamamoto and K. Takimiya, *J. Am. Chem. Soc*., 2007, **129**, 2224.

39 X.-Z. Zhu and C.-F. Chen, *J. Org. Chem.*, 2005, **70**, 917.

40 Z. Zhu and T. M. Swager, *Org. Lett*., 2001, **3**, 3471.