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ARTICLE

Palladium chloride catalyzed photochemical Heck reaction

Suresh B. Waghmode, Sudhir S. Arbuj, Bina N. Wani, and C.S. Gopinath

Abstract: $PdCl_2$ catalyzed carbon–carbon bond formation (Heck reaction) between substituted aryl halides and olefins was carried out without a ligand, under irradiation with UV–visible light. The results demonstrated that UV–visible light accelerated the rate of the reaction, leading to an excellent yield of corresponding products. The recovered palladium nanoparticles could be thermally recycled several times. $PdCl_2$ gave excellent conversion up to the fifth addition of substrate.

Key words: C–C coupling, photochemical reaction, Heck reaction, iodobenzene.

Résumé : On a effectué les réactions de Heck, formation de liaisons carbone–carbone par réactions d'halogénures d'aryles substitués et d'oléfines, catalysée par le $PdCl_2$ sans ligand, sous irradiation par de la lumière UV–visible. Les résultats démontrent que la lumière UV–visible accélère la vitesse de la réaction qui conduit à d'excellents rendements des produits correspondants. Les nanoparticules de palladium récupérées peuvent être recyclées à plusieurs reprises d'une façon thermique. Le $PdCl_2$ conduit à d'excellentes conversions, jusqu'à la cinquième addition de substrat. [Traduit par la Rédaction]

Mots-clés : couplage C–C, réaction photochimique, réaction de Heck, iodobenzène.

Introduction

The Heck reaction,[1] for the carbon–carbon (C–C) bond formation between aryl halides and olefins is an important reaction in organic chemistry.[2] It provides the simplest and most efficient way to synthesize various compounds useful in the pharmaceutical and agrochemical industries.[3] The Heck reaction tolerates various functionalities on both of the reactants. Traditionally, the Heck reactions have been carried out using 1–5 mol% palladium along with phosphine ligands in the presence of a suitable base under thermal conditions. Most of the efforts have been directed to enhance the catalytic activity of palladium by using homogeneous as well as heterogeneous reaction conditions.[4] Various ligands based on phosphorous,[5,6] nitrogen,[7] sulfur,[8] and carbene[9] have been employed successfully. However, owing to their sensitivity to the air and moisture, their toxicity, the expense, and their unrecoverable and severe reaction conditions, a ligand free Heck reaction has been developed.[10–13] Many researchers have studied the Heck reaction over a heterogeneous catalyst, such as palladium, supported on various metal oxides,[10a] silica,[10b] carbon,[10c,10d] zeolite,[10e] polyaniline,[11] polyacrylamide,[12] polyethylene glycol, and non-cross-linked polystyrene.[13] The incorporation of palladium in zeolite and ordered mesoporous materials enhances the catalytic activity and recyclability.[10e,14] Recently, simple palladium compounds such as $PdCl_2$ or $Pd(OAc)_2$, which are without any fancy ligands, have been increasingly used for the Heck reaction, owing to their low cost.[15] To increase the effectiveness of the catalyst, various techniques such as ultrasonication,[16] microwaves,[17] electrochemicals,[18] and photocatalysis[19] have also been used. Photochemical reactions have reported Heck, Suzuki–Miyaura, and Stille-type coupling reactions successively over palladium acetate and phosphine ligands.[19d,19e,19f] Recently, Chaudhary and Bedekar reported $Pd(OAc)_2$ and 1-(α-aminobenzyl) 2-naphthols, as ligands, catalyzed Mizoroki–Heck, Suzuki–Miyaura, and Sonogashira reactions under sunlight. The time taken for this reaction is very long (5–9 days[19g]) and selectivity for the trans product was considerably low. Still there is a need for the development of a new catalyst for the Heck reaction under UV–visible light irradiation (UV–vis). UV–vis energy is abundant, cheap, and the "greenest" source of energy. As we were involved in a program aimed towards the development of new strategies for C–C bond formation, we were encouraged to design a convenient and effective route to C–C bond formation under UV–vis without a ligand.[20] Herein, a UV–vis irradiated Heck reaction with various aryl iodides and olefins using $PdCl_2$ as a catalyst is revealed. Applicability of this methodology and optimization of reaction parameter is studied.

Results and discussion

The reaction between iodobenzene and ethyl acrylate under UV–vis was studied as a model system (Scheme 1). The reaction parameters were systematically optimized using various solvents, bases, and different palladium salts. In a photochemical Heck reaction, 99% conversion of iodobenzene and 9:1 selectivity for trans and cis isomers was observed in 3 h (Table 1; entry 1). The cis product was observed due to the UV–vis induced isomerization of alkenes (trans–cis).[21] To confirm whether the reaction is photochemical or thermal, the reaction was carried out without UV–vis (thermally) at 45 °C by keeping all other parameters constant. It gave only 12% conversion with 100% selectivity for the *trans*-ethyl cinnamate (Table 1; entry 2). This result shows that UV–vis exerts an influence on C–C bond formation.

Among the various solvents studied, dimethyl formamide (DMF) and dimethyl acetamide (DMAc) gave excellent conversion and selectivity for *trans*-ethyl cinnamate (Table 1; entries 1–2), whereas DMSO and acetonitrile (ACN), as solvents, gave poor yields (entries 5, 6). Under photochemical reaction conditions, it is very likely that UV–vis helps towards the formation of species intermediate between $PdCl_2$, solvent, base, and substrate, which accelerates the rate of C–C bond formation reaction. The formation of these intermediate species depends upon the nature of the nucleofuge and the C–I bond strength. The order of reactivity is

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Scheme 1. Photochemical Heck reaction between iodobenzene and ethyl acrylate.

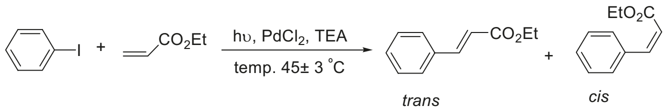


Table 1. Reaction of iodobenzene with ethyl acrylate using different solvents.

			Selectivity (%)	
Entry	Solvents	Conversion (%)	Trans	Cis
1	DMF	99	88	12
2	DMF	12	100	—
3	DMAc	99	87	13
4	NMP	87	94	6
5	DMSO	27	71	29
6	ACN	11	74	26
7	Xylene	NR	—	—

Note: Reaction conditions = iodobenzene (1 mmol), ethyl acrylate (3 mmol), triethyl amine (3 mmol), 5 mL solvent, and 0.5 mol% $PdCl_2$ were stirred for 3 h under a 400 W mercury vapour lamp at 45 ± 3 °C; NR, no reaction.

I > Br > Cl. Our efforts to characterize the intermediate species by spectroscopic methods (UV spectrometer), did not give any information, and we speculate that the half-life of the intermediate species was too small for detection. Nonpolar solvents do not show activity (entry 6). The order of activity was DMF ~ DMAc > NMP > DMSO > ACN > xylene.

The catalytic activity of different palladium sources for the C–C coupling under photochemical conditions was studied and the results are summarized in Table 2. It was observed that palladium with oxidation states 0, II, and IV were active, whereas Pd/C did not show any activity. Among the Pd salts, $PdCl_2$ showed excellent catalytic activity as well as selectivity towards the *trans*-ethyl cinnamate (Table 2 entry 1). The results of this study indicate that chloride-based Pd compounds are catalytically more active compared with other Pd compounds (Table 2). The solubility of the base affects the yield of the reaction; photochemical Heck reaction with organic bases, such as TEA and TBA, showed excellent yields compared with inorganic bases such as Na_2CO_3 and K_2CO_3. This could be attributed to the homogeneity of these bases in the reaction mixture. The study of different solvents indicated that TEA was the best among the studied bases. The effect of $PdCl_2$ concentration and UV–vis duration for the iodobenzene conversion was studied. Complete conversion was obtained within 3 h for iodobenzene; continuing the reaction increased *cis*-ethyl cinnamate with increase in irradiation time. After 25 h of irradiation the selectivity for *trans*- and *cis*-ethyl cinnamate at a ratio of 5:4 is obtained. This observation suggests that the trans product was isomerized to cis under UV–vis.[21]

The applicability of this methodology was studied for various substituted aryl iodides and olefins, and the results are summarized in Table 3. Reaction of iodobenzene with ethyl, methyl, or butyl acrylate gave satisfactory conversion and selectivity (Table 3; entries 1–3). Styrene and acryl amide (entries 4, 5) gave 46% and 10% conversion with 32% and 47% selectivity for the trans product, respectively. *Ortho*-iodophenol gave 55% conversion with 100% selectivity for the trans product (entry 6). *Ortho*- and *para*-anisole gave 50% and 85% conversion with 51% and 78% selectivity for the corresponding trans products, respectively (entries 7, 8). Generally, ortho-substituted compounds required more reaction time compared with meta- and para-substituted aryl iodides. Amino- and nitro-substituted substrates were not active under photochemical reaction conditions. Owing to the optical absorption of UV–vis by these functional groups, the rate of C–C bond formation was retarded. *Ortho*- and *para*-iodoacetanilide gave 99% and 80% conversion with 78% and 53% selectivity for the trans isomer, respectively (Table 3; entries 9, 10). The effect of substitution on various positions in an aromatic ring was studied and activity order was as follows, *ortho*- > *meta*- > *para*-iodomethylbenzoate. We found that bromo- and chloro-substituted aryl iodides gave selectively iodo-coupled products (Table 3; entries 16, 17). Disubstituted products were observed for the reaction between 1,3 di-iodobenzene and ethyl acrylate with 100% conversion showing 74% selectivity for di-substituted product (Table 3; entry 18).

Table 2. Reaction of iodobenzene with ethyl acrylate using different palladium catalysts.

			Selectivity (%)	
Sr. No.	Catalyst	Conversion (%)	Trans	Cis
1	$PdCl_2$	99	88	12
2	$Pd(OAc)_2$	53	91	9
3	$Pd(NH_3)_4Cl_2.H_2O$	55	88	12
4	$Pd(NH_3)_4(OAc)_2$	84	87	13
5	Na_2PdCl_6. 4 H_2O	92[b]	94	6
6	10% Pd/C	3	100	—
7	$[(C_6H_5)_3P]_4Pd$	43	92	8
8	$PdCl_2$ and 5% PPh_3	72	94	5

Note: Reaction conditions: iodobenzene (1 mmol), ethyl acrylate (3 mmol), triethyl amine (3 mmol), 5 mL DMF, and 0.5 mol% catalyst were stirred for 3 h under a 400 W mercury vapor lamp at 45 ± 3 °C.

[b] Time = 5 h.

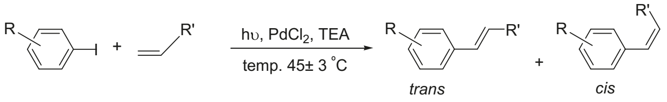
Gray colored Pd^0 nanoparticles were observed during the photochemical C–C coupling reaction. The synthesis of Pd nanoparticles was confirmed by UV–vis adsorption spectra and TEM analysis (see the Supplementary data). The UV spectrum of $PdCl_2$ in DMF showed absorbance at 422 nm, owing to d–d transitions,[22] whereas Pd^0 did not show surface plasmon bands in the UV–vis range.[23] TEM analysis showed cubic crystalline structure of palladium particles with a size of 120 ± 10 nm (see the Supplementary data). X-ray diffraction pattern of the Pd nanoparticles was recorded, and were found to match earlier reports (JCPDS No. 46-1043).[24] The observed binding-energy values of Pd $3d_{5/2}$ and $3d_{3/2}$ core levels were 335.3 and 340.7 eV, respectively[25]. X-ray photoemission spectra confirmed the formation of Pd^0 particles. Some Pd^{2+} was also observed at 336.5 eV, attributed to unreacted $PdCl_2$.

After the completion of the reaction, Pd nanoparticles were recovered by centrifugation and washed several times with DMF. These nanoparticles were not active under photochemical reaction conditions, which suggest that the oxidative insertion of metallic palladium into iodobenzene to form an intermediate species was not possible under the photochemical reaction conditions, whereas $PdCl_2$ easily formed the intermediate species. However, the recovered palladium nanoparticles were thermally recycled at 130 °C, and the catalytic activity was found to be same, even for the sixth recycle (Supplementary data). Further, to study the recyclability of $PdCl_2$ towards the photochemical Heck reaction, we carried out the reaction using iodobenzene and ethyl acrylate. After completion of the reaction first cycle, in the first addition, all of the reactants except $PdCl_2$ were added to the earlier reaction mixture, and the reaction was continued for 3 h. This gave an excellent conversion up to the fifth addition of reagents (see the Supplementary data).

Conclusions

In conclusion, we have developed a simple $PdCl_2$-catalyzed photochemical C–C coupling reaction for various substituted aryl iodides and olefins that favors a good yield for the corresponding coupled products at ambient reaction conditions. The Heck reaction gave minor amounts of cis product, owing to photochemical isomerization of the initially formed trans product. Polar aprotic solvents gave excellent yields of the desired product, compared with nonpolar solvents. Chloride-based Pd sources were more cat-

Table 3. The photochemical Heck coupling of aryl halides and olefins using $PdCl_2$.



R- H, OH, OMe, NHCOMe, CO_2Me, COMe, Cl, Br, I
R′- Ph, CO_2Me, CO_2Et, CO_2Bu, CO_2NH_2

					Selectivity (%)	
Entry	R	X	R′	Conversion (%)	Trans	Cis
1	H	I	CO_2Et	99	88	12
2	H	I	CO_2Me	99	89	11
3	H	I	$CO_2{}^nBu$	100^b	78	22
4	H	I	Ph	46^b	32	68
5	H	I	$CONH_2$	10^b	47	53
6	2-OH	I	CO_2Et	55^b	100	—
7	2-OMe	I	CO_2Et	50^b	51	49
8	4-OMe	I	CO_2Et	100^b	64	36
9	2-NHCOMe	I	CO_2Et	99^c	78	22
10	4-NHCOMe	I	CO_2Et	80^c	53	47
11	2-CO_2Me	I	CO_2Et	100^b	77	23
12	3-CO_2Me	I	CO_2Et	84^c	84	16
13	4-CO_2Me	I	CO_2Et	70^c	88	12
14	4-COMe	Br	CO_2Et	NR	—	—
15	4-COMe	I	CO_2Et	79^c	91	9
16	4-Br	I	CO_2Et	100^b	63	37
17	4-Cl	I	CO_2Et	85^b	79	21
18	3-I	I	CO_2Et	100^b	$74^{\#}$	19

Note: Reaction conditions = substrate (1 mmol), olefin (3 mmol), triethylamine (3 mmol), 5 mL DMF, and 0.5 mol% $PdCl_2$ were stirred for 3 h under a 400 W (mercury vapour lamp) UV-visible light irradiation at 45 ± 3 °C.

[b] Reaction time = 5 h.

[c] Reaction time = 7 h.

[#] Di-substituted trans compound.

alytically active compared with other Pd sources. Organic bases were superior to inorganic bases. We believe that during the reaction, $PdCl_2$ easily formed intermediate species with iodobenzene, solvent, base, and reagent, which accelerated the rate of reaction. Recovered palladium nanoparticles were unable to form intermediate species, which formed with $PdCl_2$ upon UV–vis. The recovered palladium nanoparticles were easily separated and reused several times as a heterogeneous catalyst under thermal Heck reaction conditions without significant loss of catalytic activity. The $PdCl_2$ was active up to the fifth addition of all the reagents.

Experimental section

General procedure for the photochemical Heck reaction

To a 25 mL round bottom flask 1 mmol of aryl iodide, 3 mmol of olefin, 3 mmol of triethyl amine (TEA) in dimethyl formamide (DMF; 5 mL) were mixed, and to this mixture 1 mg of $PdCl_2$ was added. The resulting reaction mixture was irradiated under a 400 W mercury vapor lamp with continuous stirring in a closed box, free from stray light. The reaction temperature was measured directly in a reaction vessel. The mercury vapor lamp was kept vertically in the quartz tube, which was equipped with the cold water circulation system to minimize the heating effect. The progress of the reaction was monitored by GC (HP-5890) equipped with capillary column (HP-5, 30 m × 0.32 mm × 0.25 μm). After completion, the reaction mixture was diluted with water (10 mL) and the products were extracted using ethyl acetate (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate and purified by using column chromatography over silicagel [hexane or hexane/ethyl acetate (9:1)]. The GC–MS spectra were taken with a Shimadzu QP-5050 equipped with TCD and a capillary column (DB-5). FTIR spectra were recorded in Nujol mull on a Shimadzu 8400 and are expressed in cm^{-1}. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$ using a Varian mercury spectrometer. XPS measurements were made with a VG ESCALAB 3000 at room temperature, and MgKα X-ray radiation was employed.[26]

Supplementary data

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2012-0377.

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References

(1) (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press, London, **1985**; (b) Tsuji, J. *Palladium Reagents and Catalysis*; Wiley. Chiehester, **1995**; (c) Heck, R. F.; and Nolley, J. P., Jr. *J. Org. Chem.* **1972**, *37*, 2320. doi:10.1021/jo00979a024.

(2) (a) Dounay, A. M.; Overman, L. E. *Chem. Rev.* **2003**, *10–3*, 2945. doi:10.1021/cr020039h; (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. doi:10.1021/cr9903048; (c) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2. doi:10.1021/ar00049a001; (d) Djakovitch, L.; Koehler, K. *J. Am. Chem. Soc.* **2001**, *123*, 5990. doi:10.1021/ja001087r; (e) Imbos, R.; Minnaard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2002**, *124*, 184. doi:10.1021/ja017200a; (f) Castella, M.; Calahorra, F.; Sainz, D.; Velasco, D. *Org. Lett.* **2001**, *3*, 541. doi:10.1021/ol000370s.

(3) Zapf, A.; Beller, M. *Top. Catal.* **2002**, *19*, 101. doi:10.1023/A:1013889401432.

(4) (a) Phan, N. T. S.; Sluys, M. V. D.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609. doi:10.1002/adsc.200505473; (b) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553. doi:10.1002/adsc.200404178.

(5) (a) Stambuli, J. P.; Stauffer, S. R.; Shaughnessy, K. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 2677. doi:10.1021/ja0058435; (b) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989. doi:10.1021/ja010988c; (c) Jeffery, T. *Tetrahedron Lett.* **1994**, *35*, 3051. doi:10.1016/S0040-4039(00)76825-0.

(6) (a) Herrmann, W. A.; Brossmer, C. O.; Reisinger, C. K.; Priermeier, T.; Beller, M.; Fisher, H. *Angew. Chem., Int. Ed.* **1995**, *34*, 1844. doi:10.1002/anie.199518441; (b) Ohff, M.; Ohff, A.van der ; Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. doi:10.1021/ja9729692.

(7) Gai, X.; Grigg, R.; Ramzan, M. I.; Sridharan, V.; Collard, S.; Muir, J. E. ; *Chem. Commun.* 2000, 2053. doi:10.1039/B005452F.

(8) Dai, M.; Liang, B.; Wang, C.; Chen, J.; Yang, Z. *Org. Lett.* **2004**, *6*, 221. doi:10.1021/ol036182u.

(9) Andrus, M. B.; Song, C.; Zhang, J. *Org. Lett.* **2002**, *4*, 2079. doi:10.1021/ol025961s.

(10) (a) Wagner, M.; Kohler, K.; Djakovitch, L.; Weinkauf, S.; Hagen, V.; Muhler, M. *Top. Catal.* **2000**, *13*, 319. doi:10.1023/A:1009022030636; (b) Polshettiwar, V.; Molnar, A. *Tetrahedron* **2007**, *63* 6949. doi:10.1016/j.tet.2007.04.023; (c) Heidenreich, R.; Krauter, J. G. E.; Pietsch, J.; Kohler, K. *J. Mol. Catal. A: Chem.* 2002, 182–*183*, 499. doi:10.1016/S1381-1169(01)00499-X; (d) Zhao, F.; Shirai, M.; Ikushima, Y.; Arai, M. *J. Mol. Catal. A: Chem.* **2002**, *180*, 211. doi:10.1016/S1381-1169(01)00436-8; (e) Djakovitch, L.; Kohler, K. *J. Am. Chem. Soc.* **2001**, *123*, 5990. doi:10.1021/ja001087r.

(11) Kantam, L. M.; Roy, M.; Roy, S.; Sreedhar, B.; Madhavendra, S. S.; Choudary, B. M.; De, R. L. ; *Tetrahedron* **2007**, *63*, 8002. doi:10.1016/j.tet.2007.05.064.

(12) Mahdavi, H.; Zirakzadeh, A.; Amani, J. *React. Funct. Polym.* **2007**, *67*, 716. doi:10.1016/j.reactfunctpolym.2007.05.006.

(13) (a) Kollhofer, A.; Plenio, H. *Chem. A Eur. J.* **2003**, *9*, 1416. doi:10.1002/chem.200390161; (b) Datta, A.; Ebert, K.; Plenio, H. *Organometallics* **2003**, *22*, 4685; (c) Lin, C. A.; Luo, F. T. *Tetrahedron Lett.* **2003**, *44*, 7565. doi:10.1016/j.tetlet.2003.08.069; (d) Leyva, A.; Garcia, H.; Corma, A. *Tetrahedron* **2007**, *63*, 7097. doi:10.1016/j.tet.2007.05.008.

(14) Papp, A; Galbacs, G.; Molnar, A. *Tetrahedron Lett.* **2005**, *46*, 7725. doi:10.1016/j.tetlet.2005.09.048.

(15) Reetz, M. T.; Westermann, E. *Angew. Chem. Int. Ed.* **2000**, *39*, 165. doi:10.1002/(SICI)1521-3773(20000103)39:1<165::AID-ANIE165>3.0.CO;2-B.

(16) (a) Zhang, Z.; Zha, Z.; Gan, C.; Pan, C.; Zhou, Y.; Wang, Z.; Zhou, M. M. *J. Org. Chem.* **2006**, *71*, 4339. doi:10.1021/jo060372b; (b) Ambulgekar, G. V.; Bhanage, B. M.; Samant, S. D. *Tetrahedron Lett.* **2005**, *46*, 2483. doi:10.1016/j.tetlet.2005.02.035.

(17) (a) Du, L. H.; Wang, Y. G. *Synth. Commun.* **2007**, *37*, 217. doi:10.1080/00397910601031801; (b) Dawood, K. M. *Tetrahedron* **2007**, *63*, 9642. doi:10.1016/j.tet.2007.07.029; (c) Arvela, R. K.; Leadbeater, N. E.; Collins, M. J., Jr. *Tetrahedron* **2005**, *61*, 9349. doi:10.1016/j.tet.2005.07.063.

(18) Tian, J.; Moeller, K. D. *Org. Lett.* **2005**, *7*, 5381. doi:10.1021/ol0519487.

(19) (a) Tsubomura, T.; Sakai K. *Coord. Chemistry Rev.* **1998**, *171*, 107. doi:10.1016/S0010-8545(98)90019-4; (b) Hennig, H. *Coordination Chemistry Rev.* **1999**, *182*, 101. doi:10.1016/S0010-8545(98)00201-X; (c) Osawa, M.; Nagai, H.; Akita, M. *Dalton Trans.* **2007**, *827* and references therein. doi:10.1039/B618007H; (d) Imperato, G.; Kcnig, B. *ChemSusChem* **2008**, *1*, 993. doi:doi:10.1002/cssc.200800187; (e) Fredricks, M. A.; Drees, M.; Köhler, K. *ChemCatChem* **2010**, *2*, 1467 and references therein. doi:10.1002/cctc.201000137; (f) Oliveira, M. S.; Severino, D.; Prado, F. M.; Angeli, J. P. F.; Motta, F. D.; Baptista, M. S.; Medeiros, M. H. G.; Mascio, P. D. *Photochem. Photobiol. Sci.* **2011**, *10*, 1546. doi:10.1039/C1PP05120B; (g) Chaudhary, A.R.; Bedekar, A. V. *Tetrahedron Lett.* doi:doi:10.1016/j.tetlet.2012.08.139.

(20) (a) Borhade, S. R.; Waghmode, S. B. *Ind. J. Chem., Sect. B* **2008**, *47*, 1549; (b) Borhade, S. R.; Waghmode , *Can. J. Chem.* **2011**, *89*, 1355. doi:10.1139/v11-103; (c) Waghmode, S. B.; Wagholikar, S. G.; Sivasankar, S. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1989. doi:10.1246/bcsj.76.1989; (d) Borhade, S. R.; Waghmode, S. B. *Tetrahedron Lett.* **2008**, *49*, 3423. doi:10.1016/j.tetlet.2008.03.109; (e) Borhade, S. R.; Waghmode, S. B. *Beilstein J. Org. Chem.* **2011**, *7*, 310. doi:10.3762/bjoc.7.41.

(21) (a) Kahnt, G. *Phytochemistry* **1967**, *6*, 755. doi:10.1016/S0031-9422(00)86017-3; (b) Wyman, G.M. *Chem. Rev.* **1955**, *55*, 625. doi:10.1021/cr50004a001.

(22) (a) Elding, L. I.; Olsson, L. F. *J. Phys. Chem.* **1978**, *82*, 69. doi:10.1021/j100490a018; (b) Luo, C.; Zhang, Y.; Wang, Y. *J. Mol. Catal. A: Chem.* **2005**, *229*, 7. doi:10.1016/j.molcata.2004.10.039.

(23) Cliffel, D. E.; Zamborini, F. P.; Gross, S. M.; Murray, R. W. *Langmuir* **2000**, *16*, 9699. doi:10.1021/la000922f.

(24) Zheng, L.; Li, J. *J. Phys. Chem. B* **2005**, *109*, 1108. doi:10.1021/jp0456234.

(25) (a) Lengke, M. F.; Fleet, M. E.; Southam, G. *Langmuir* **2007**, *23*, 8982. doi:10.1021/la7012446; (b) Narayana, M.; Michalik, J.; Contarini, S.; Kevan, L. *J. Phys. Chem.* **1985**, *89*, 3895. doi:10.1021/j100264a026.

(26) (a) Joly, V. L. J.; Joy, P. A.; Date, S. K.; Gopinath, C. S. *J. Phys. Cond. Matt.* **2001**, *13*, 649. doi:10.1088/0953-8984/13/4/311; (b) Gopinath, C. S.; Subramanian, S.; Prabhu, P. S.; Rao, M. S. R.; Subba Rao, G. V. *Physica C* **1993**, *218*, 117. doi:10.1016/0921-4534(93)90274-T; (c) Murugan, B.; Srinivas, D.; Gopinath, C. S.; Ramaswamy, V.; Ramaswamy, A. V. *Chem. Mater.* **2005**, *17*, 3983. doi:10.1021/cm050401j.