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# A portable light-delivery device for *in situ* photocrystallographic experiments in the home laboratory

**Radosław Kamiński,* Katarzyna N. Jarzembska,* Sylwia E. Kutyła and Marek Kamiński**

Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, Warsaw, 02-089, Poland. *Correspondence e-mail: rkaminski@chem.uw.edu.pl, katarzyna.jarzembska@gmail.com

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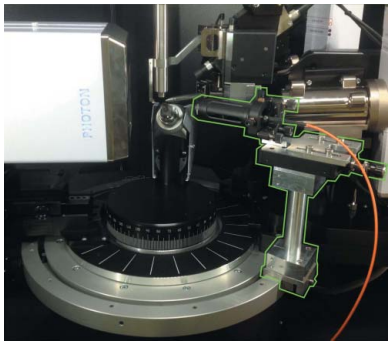
Photocrystallographic experiments provide valuable information on how crystalline samples interact with light, yielding light-induced structural changes. Studied processes include, among others, solid state chemical reactions, as well as isolation and characterization of various metastable states. Thus, some instrumentation development efforts in the field have been dedicated to facilitating such experiments using a home X-ray source. In this contribution, a portable, easy-to-use and adjustable light-delivery device for home single-crystal diffractometers is described. The whole system consists of adjustable laser-focusing optics and a holder, which can be conveniently attached to a goniometer, as an additional sample conditioning device. The light-delivery device was designed to reduce any goniometer movement limitations. It allows one to conveniently perform photocrystallographic experiments without violation of the X-ray safety protocols, even when changing the light source is necessary. Test *in situ* photocrystallographic experiments performed on the literature-reported $Ni(NO_2)_2(dppe)$ complex [dppe is bis(diphenylphosphino)-ethane] confirm the effectiveness and applicability of the device for conducting linkage isomer single-crystal-to-single-crystal transformations.

## 1. Introduction

Knowledge about light-induced structural changes provides a great amount of information on the mechanisms of the studied processes, on the nature of metastable states *etc.* In this respect, single crystals are very suitable experimental objects, being characterized by a well defined three-dimensional structure, which facilitates the detection of even subtle changes in the atomic order. Furthermore, solid-state materials applications are also of constantly increasing significance. These range from solid-state sensors, light-controlled mechanical systems, optoelectronic devices and ultra-high-capacity data storage media, to environmental and biomedical applications (Shepherd *et al.*, 2013; Cole, 2008; Zhang *et al.*, 2013). Investigations of light-induced transformations in the solid state constitute a domain of photocrystallography (Coppens, 2003). Recent studies in the field include both reversible and irreversible processes, such as light-induced single-crystal-to-single-crystal transformations (isomerization reactions (Zheng *et al.*, 2008), spin-crossover interconversions (Cailleau *et al.*, 2010; Létard *et al.*, 2012), linkage isomerism (*e.g.* Kovalevsky *et al.*, 2003; Hatcher, 2016; Warren *et al.*, 2014; Sylvester *et al.*, 2014), chemical reactions (*e.g.* [2 + 2] photodimerizations; Benedict & Coppens, 2009; Hallmann *et al.*, 2009), ring-closing reactions (Jean-Ruel *et al.*, 2011; Cox *et al.*, 2015; Brayshaw *et al.*, 2011), photoeliminations (*e.g.* Powers *et*



*al.*, 2014), charge transfer (Coppens, 2011; Coppens *et al.*, 2010; Hatcher & Raithby, 2014; Jarzembska *et al.*, 2014; Trzop *et al.*, 2014), photo-biochemical cycles (Ren *et al.*, 1999) and others.

Naturally, it is most convenient to conduct photocrystallographic experiments by irradiating crystals that are already mounted on a goniometer. This allows full control of the sample and easy measurement automation. Appropriate instrumentation solutions have already been implemented at synchrotron sources (Chen *et al.*, 2014; Graber *et al.*, 2011; Nowell *et al.*, 2012; Hoshino *et al.*, 2015) and have enabled steady-state and pump–probe photocrystallographic experiments. Nevertheless, since synchrotron time is limited, in cases where a very high X-ray flux is not necessary, it can be helpful to use a home laboratory setup. At a home diffractometer, however, there is much less free space around a sample, partly owing to safety reasons (X-ray radiation enclosure). Some of the most recent examples of home photocrystallographic experiments include applications of a diode laser (Casaretto *et al.*, 2015) or a mercury lamp (Konieczny *et al.*, 2016) (with a set of filters) to irradiate a crystal directly in the diffractometer. Unfortunately, no details on how the light beam was directed onto the sample were given by these authors.

One of the first fully described devices for crystal *in situ* irradiation on a laboratory diffractometer was developed by Brayshaw *et al.* (2010), who designed a light-emitting diode (LED) ring mounted on an open-flow low-temperature device. Despite its success, this design has several disadvantages, such as restricted detector angles, lack of flexibility in choosing the light wavelength and limited power delivered onto the sample. These limitations can be overcome using the approach presented by Cox *et al.* (2015). According to their description, the light-delivery device is based on optical fibres, transferring light into a diffractometer enclosure, and concise focusing optics assemblies containing fused silica lenses. In addition, the primary beam is split in two using a bifurcated fibre bundle, thus ensuring the homogeneity of the light irradiation. However, the described device is permanently mounted inside the diffractometer enclosure and cannot be easily adjusted.

Hence, in this contribution we present our design of a portable light-delivery device. We followed the idea of Cox *et al.* (2015) and developed it further by several useful and important mechanical solutions, facilitating light-beam alignments and photocrystallographic experiments.

## 2. Design and construction details

The designed light-delivery device consists of several elements: the mounting part, a tower, an adjustable stage and plate, and kinematic mounts which hold/support the focusing optics. A photograph of the device is presented in Fig. 1, while side and top technical views are shown in Fig. 2.

(i) The whole light-delivery device has primarily been designed to work best with Bruker AXS laboratory diffractometers (Fig. 1), which have a characteristic metal ring attached to the main goniometer body. A curved clamp-like part was designed to fit this ring and allow for convenient mounting, relocation and dismounting of the device on a diffractometer (without losing the beam alignment – the

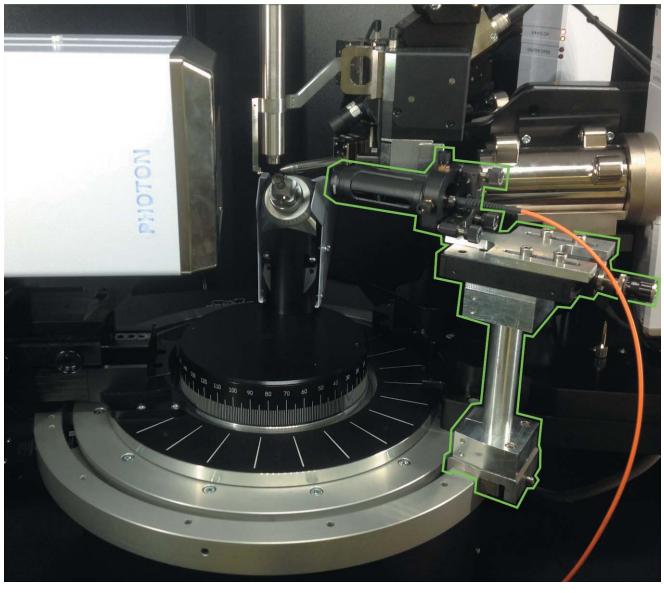



**Figure 1**
The designed light-delivery device (outlined in green) mounted onto the dual-source Bruker AXS diffractometer. The orange cable is the fibre optics attached to the LED source (not shown) outside the diffractometer enclosure. In the current example the device is mounted next to the Cu source, allowing high-resolution experiments with Mo radiation. Alternatively, the device can be mounted on the other side (next to the Mo source) to accommodate experiments with Cu radiation to the highest possible resolution.

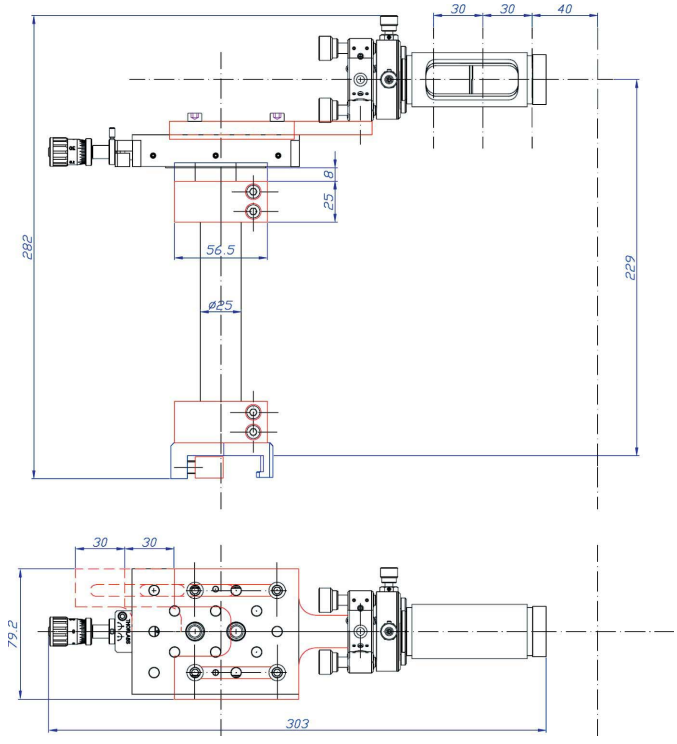



**Figure 2**
Side and top views of the design, showing selected dimensions (in mm). Both views also indicate possible translations of the top mounting plate with the optics assembly.

device is sufficiently stable/rigid). A tower with a metal grip is attached to the clamp. The tower is basically a metal rod of a specified length tailored to match a particular diffractometer. The clamp was made of steel (to withstand the applied load), while the remaining home-machined parts were made of aluminium.

(ii) A Thorlabs translation stage equipped with a differential adjuster screw (catalogue No. PT1A/M; 25 mm travel range) is located on top of the above-described tower and attached by a metal grip. The translation stage is attached to the mounting plate, which allows for further distance adjustments of the optical part. The optics assembly is screw-mounted to the end of the plate and consists of a Thorlabs five-axis kinematic mount (catalogue No. K5X1), a lens tube, and collimating and focusing lenses. The construction enables precise light focusing on the sample through kinematic mount adjustments. Since the experimental requirements may vary, the tube total length is adjustable, and various desired optical elements may be used (other lenses with different focal lengths, filters, polarizers *etc.*). The mounting plate can also be placed at various distances (Fig. 2). The precise adjustment of the focal spot distance can be achieved by rotating the translation stage screw. In general, the whole device was designed to allow considerable flexibility.

(iii) The LED/laser light is delivered to the optics assembly through a fibre optic cable [as in the case described by Cox *et al.* (2015)]. The fibre is connected to the assembly and the LED source through standard SMA connectors. Depending on experimental requirements, the user can choose between various types of fibre optics. We note that fibre optics can handle more powerful laser light, which enables one to conduct photocrystallographic experiments based on two-photon absorption phenomena (Benedict & Coppens, 2009; Harada *et al.*, 2008).

(iv) The auxiliary part (not shown in Fig. 1) is a controlled electronic power supply capable of driving the Thorlabs LEDs. The box has been designed to ensure further flexibility of the experiment if any modifications are needed [*e.g.* automation of the data collection procedures as described by Hatcher & Raithby (2014)].

Finally, it should be stressed that the whole assembly has been designed to minimize any interference with the goniometer movements. In the case of our example experiment, the device has been mounted right next to the X-ray source. Thus, only a small additional limit for the detector swing angle needed to be applied to avoid collisions. The device does not collide with a fixed-$\chi$ Bruker AXS goniometer and requires solely some restrictions on the $\kappa$ angle in the case of a four-circle Bruker AXS goniometer. Such features enable one to use the device in high-resolution crystallographic studies of metastable states in crystals (Pillet *et al.*, 2008). Another important feature is that the light source and other accessories can be installed outside the diffractometer safety enclosure. Thereby, light sources can be seamlessly exchanged (*e.g.* for photo-switching experiments), with no harm to the pre-set sample environment and the running X-ray diffraction experiment. In the case of laser sources this is especially important because of the size of the laser boxes and heat dissipation issues.

## 3. Example application

The performance of the designed device was tested on the well known case of $NO_2$-linkage isomers of nickel(II) complexes (Hatcher & Raithby, 2013). For the purpose of this study we chose the previously reported Ni($NO_2$)$_2$}(dppe) complex [dppe is bis(diphenylphosphino)ethane], in which the N-bound nitrite ligand switches to its O-bound metastable isomer upon near-UV light irradiation (Warren *et al.*, 2014). The published article on this topic reports the use of six 400 nm LED sources mounted onto the ring (Brayshaw *et al.*, 2010). In our case, a 365 nm Thorlabs fibre-coupled LED (catalogue No. M365F1) was applied. The light was delivered through a 10 m multimode fibre optic cable (0.22 numerical aperture, 400 µm core diameter, solarization resistant with polyimide coating; Thorlabs catalogue No. UM22-400) and then focused onto the sample with the optics described in the preceding section (UV fused silica uncoated lenses). The examined crystal was irradiated for approximately 50 min with the LED light produced with the driving current set to 50 mA. During this process the crystal was slowly rotated to ensure the uniformity of the sample irradiation. The crystal turned dark after only 10 min of exposure (Fig. 3). We note here that the use of more intense light (LED driving current set to >100 mA) resulted in a faster deterioration of the crystal.

X-ray diffraction experiments were performed before and after irradiation. The first experiment was conducted in the dark to determine the structure of the ground state, whereas the aim of the second experiment, carried out after the LED irradiation, was to capture the structure of the metastable state. Both experiments were performed at 120 K, as the metastable state is known to exist at this temperature (the metastable ONO isomer reverts back to the $NO_2$ isomer above 180 K). Fig. 4 shows the X-ray structures of both isomers, and confirms the applicability and efficiency of our light-delivery device in triggering light-induced transformations in the solid state. As anticipated, the transformation was driven to 100%,

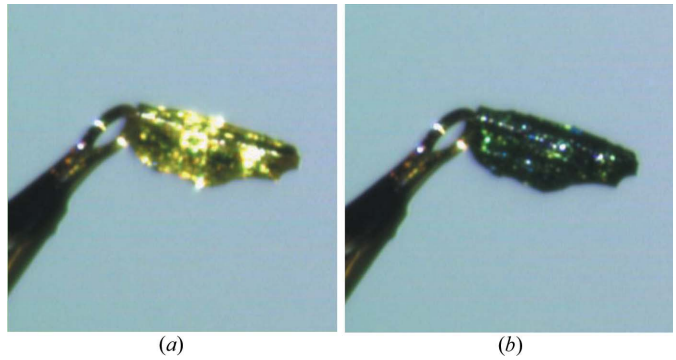



**Figure 3**
Single crystal of Ni($NO_2$)$_2$(dppe) before (*a*) and after (*b*) LED ($\lambda$ = 365 nm) irradiation for about 15 min.

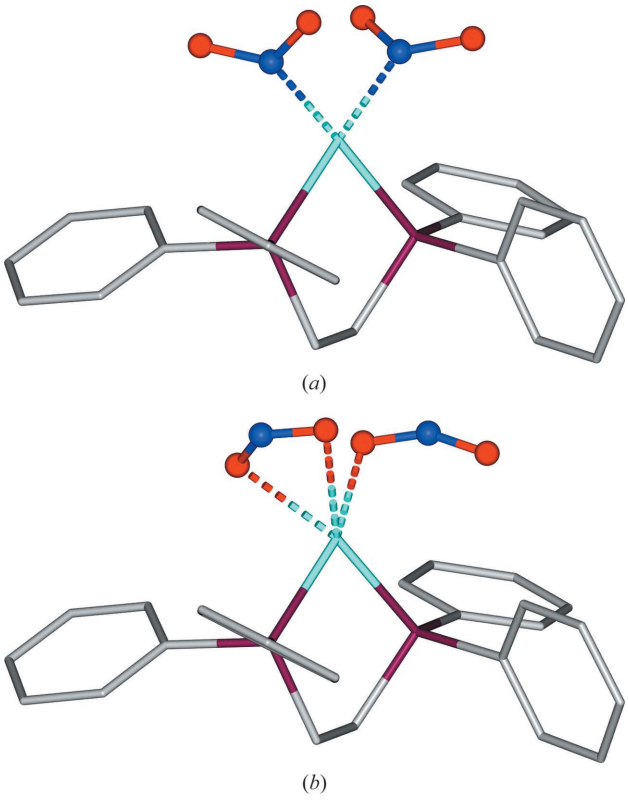



**Figure 4**
X-ray-determined molecular structures of $Ni(NO_2)_2$(dppe) before (*a*) and after (*b*) LED (λ = 365 nm) irradiation for about 50 min.

which is consistent with the earlier mentioned literature report (Warren *et al.*, 2014).

## 4. Summary

In this short contribution we have described the design and example performance of a portable light-delivery device for applications in *in situ* photocrystallographic experiments using a home X-ray diffractometer. The presented device facilitates light irradiation of a sample mounted in a diffractometer. Our design has several advantages over other known solutions, mainly in terms of flexibility (convenient mounting of the device, variety of alignment options *etc.*). We also paid a lot of attention to minimizing any limitations of the goniometer movements. The device is designed to work best with Bruker AXS laboratory diffractometers, but will be equally applicable for diffraction setups from other vendors after only minimal changes to mechanical components. The light (either from an LED or a laser) is delivered through fibre optics to the device. Homogenous sample illumination can be achieved by rotation of the sample, or facilitated by placing two such devices in different positions.

Finally, we have shown that our device performs well in photocrystallographic linkage isomer transformation experiments. We note that the full analysis of diffraction data for other new samples will be presented shortly. We believe the design will also be useful for performing of other kinds of *in situ* photocrystallographic experiments at a home laboratory.

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## References

Benedict, J. B. & Coppens, P. (2009). *J. Phys. Chem. A*, **113**, 3116–3120.
Brayshaw, S. K., Knight, J. W., Raithby, P. R., Savarese, T. L., Schiffers, S., Teat, S. J., Warren, J. E. & Warren, M. R. (2010). *J. Appl. Cryst.* **43**, 337–340.
Brayshaw, S. K., Schiffers, S., Stevenson, A. J., Teat, S. J., Warren, M. R., Bennett, R. D., Sazanovich, I. V., Buckley, A. R., Weinstein, J. A. & Raithby, P. R. (2011). *Chem. Eur. J.* **17**, 4385–4395.
Cailleau, H., Lorenc, M., Guérin, L., Servol, M., Collet, E. & Buron-Le Cointe, M. (2010). *Acta Cryst.* A**66**, 189–197.
Casaretto, N., Pillet, S., Bendeif, E.-E., Schaniel, D., Gallien, A. K. E., Klüfers, P. & Woike, T. (2015). *Acta Cryst.* B**71**, 788–797.
Chen, Y.-S., Brewer, H., Meron, M. & Viccaro, J. (2014). *Acta Cryst.* A**70**, C1727.
Cole, J. M. (2008). *Acta Cryst.* A**64**, 259–271.
Coppens, P. (2003). *Chem. Commun.* pp. 1317–1320.
Coppens, P. (2011). *J. Phys. Chem. Lett.* **2**, 616–621.
Coppens, P., Benedict, J., Messerschmidt, M., Novozhilova, I., Graber, T., Chen, Y.-S., Vorontsov, I., Scheins, S. & Zheng, S.-L. (2010). *Acta Cryst.* A**66**, 179–188.
Cox, J. M., Walton, I. M., Patel, D. G., Xu, M., Chen, Y.-S. & Benedict, J. B. (2015). *J. Phys. Chem. A*, **119**, 884–888.
Graber, T. *et al.* (2011). *J. Synchrotron Rad.* **18**, 658–670.
Hallmann, J., Morgenroth, W., Paulmann, C., Davaasambuu, J., Kong, Q., Wulff, M. & Techert, S. (2009). *J. Am. Chem. Soc.* **131**, 15018–15025.
Harada, J., Nakajima, R. & Ogawa, K. (2008). *J. Am. Chem. Soc.* **130**, 7085–7091.
Hatcher, L. E. (2016). *CrystEngComm*, **18**, 4180–4187.
Hatcher, L. E. & Raithby, P. R. (2013). *Acta Cryst.* C**69**, 1448–1456.
Hatcher, L. E. & Raithby, P. R. (2014). *Coord. Chem. Rev.* **277–278**, 69–79.
Hoshino, M., Adachi, S. & Koshihara, S. (2015). *CrystEngComm*, **17**, 8786–8795.
Jarzembska, K. N., Kamiński, R., Fournier, B., Trzop, E., Sokolow, J. D., Henning, R., Chen, Y. & Coppens, P. (2014). *Inorg. Chem.* **53**, 10594–10601.
Jean-Ruel, H., Cooney, R. R., Gao, M., Lu, C., Kochman, M. A., Morrison, C. A. & Miller, R. J. D. (2011). *J. Phys. Chem. A*, **115**, 13158–13168.
Konieczny, K., Bąkowicz, J. & Turowska-Tyrk, I. (2016). *J. Chem. Crystallogr.* **46**, 77–83.

Kovalevsky, A. Y., Bagley, K. A., Cole, J. M. & Coppens, P. (2003). *Inorg. Chem.* **42**, 140–147.
Létard, J.-F., Asthana, S., Shepherd, H. J., Guionneau, P., Goeta, A. E., Suemura, N., Ishikawa, R. & Kaizaki, S. (2012). *Chem. Eur. J.* **18**, 5924–5934.
Nowell, H., Barnett, S. A., Christensen, K. E., Teat, S. J. & Allan, D. R. (2012). *J. Synchrotron Rad.* **19**, 435–441.
Pillet, S., Legrand, V., Weber, H.-P., Souhassou, M., Létard, J.-F., Guionneau, P. & Lecomte, C. (2008). *Z. Kristallogr.* **223**, 235–249.
Powers, D. C., Anderson, B. L., Hwang, S. J., Powers, T. M., Pérez, L. M., Hall, M. B., Zheng, S.-L., Chen, Y.-S. & Nocera, D. G. (2014). *J. Am. Chem. Soc.* **136**, 15346–15355.
Ren, Z., Bourgeois, D., Helliwell, J. R., Moffat, K., Šrajer, V. & Stoddard, B. L. (1999). *J. Synchrotron Rad.* **6**, 891–917.
Shepherd, H. J., Gural'skiy, I. A., Quintero, C. M., Tricard, S., Salmon, L., Molnár, G. & Bousseksou, A. (2013). *Nat. Commun.* **4**, 1–9.
Sylvester, S. O., Cole, J. M., Waddell, P. G., Nowell, H. & Wilson, C. (2014). *J. Phys. Chem. C*, **118**, 16003–16010.
Trzop, E., Fournier, B., Jarzembska, K., Sokolow, J., Kaminski, R., Benedict, J., Chen, Y., Henning, R. & Coppens, P. (2014). *Acta Cryst.* A**70**, C776.
Warren, M. R., Easun, T. L., Brayshaw, S. K., Deeth, R. J., George, M. W., Johnson, A. L., Schiffers, S., Teat, S. J., Warren, A. J., Warren, J. E., Wilson, C. C., Woodall, C. H. & Raithby, P. R. (2014). *Chem. Eur. J.* **20**, 5468–5477.
Zhang, J., Zou, Q. & Tian, H. (2013). *Adv. Mater.* **25**, 378–399.
Zheng, S.-L., Pham, O., Vande Velde, C. M. L., Gembicky, M. & Coppens, P. (2008). *Chem. Commun.* pp. 2538–2540.